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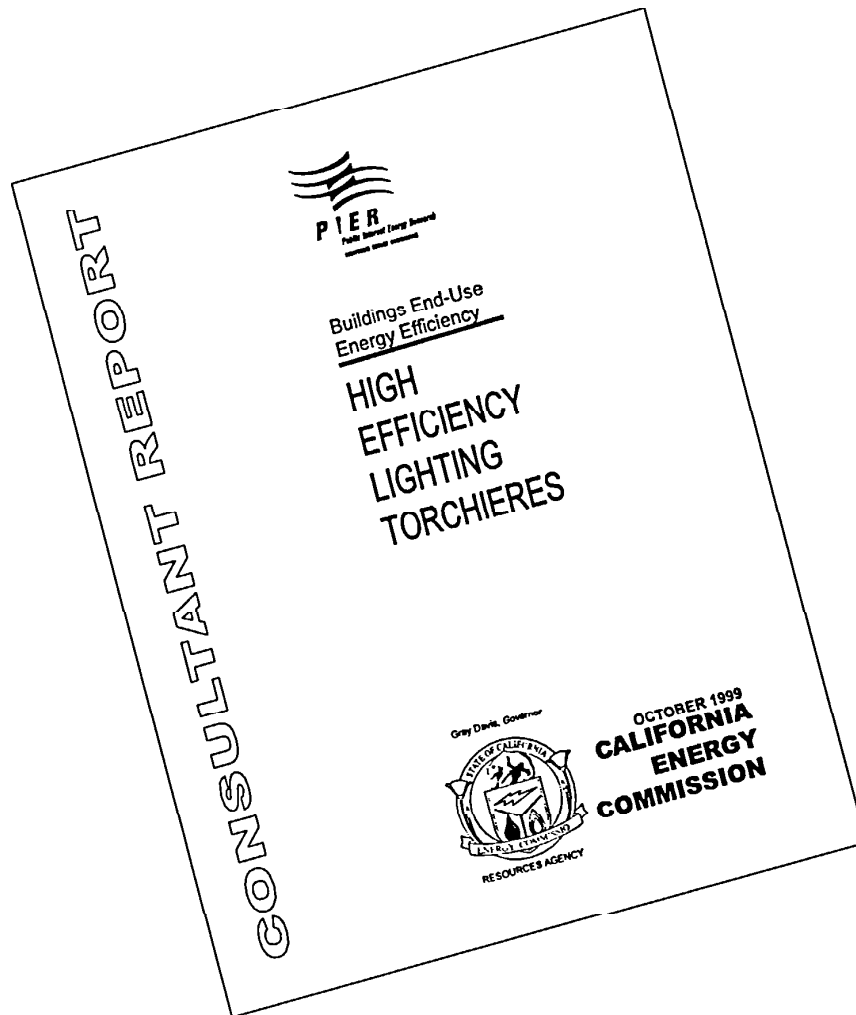
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Appendix D	Karamchandani, P., Zhang, Y., and C. Seigneur, 1999. Simulation of Sulfate Formation in the Mohave Power Plant Plume. Report prepared for the Electric Power Research Institute, January.
Appendix E	Lowenthal, D., J.G. Watson, and P. Saxena, 1999. Contributions to Light Extinction During Project MOHAVE, submitted to <i>Atmospheric Environment</i> , September.
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Appendix G	Project MOHAVE Final Report Independent Peer Review Comments.

- Appendix H. ENSR Corporation, 1999. "Extent of Visual Impairment in California." Report prepared for Southern California Edison Company, June.
- Appendix I Santos, L., Sykes, R. I., Karamchandani, P., Seigneur, C., Lurmann, F., and R. Arndt, 1999: Second-order Puff Model with Aqueous-Phase Chemistry and Aerosols, Draft Final Report prepared for EPRI, SCE, and California Energy Commission.
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- Appendix J Babich, P., Wang, P-Y., Allen, G., Sioutas, C. and P. Koutrakis, 1999: Development and Evaluation of a Continuous PM_{2.5} Mass Monitor, submitted to *Aerosol Science and Technology*, July.
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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliability energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million through the Year 2001 to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research.

In 1998, the Commission awarded approximately \$17 million to 39 separate transition RD&D projects covering the five PIER subject areas. These projects were selected to preserve the benefits of the most promising ongoing public interest RD&D efforts conducted by investor-owned utilities prior to the onset of electricity restructuring.

What follows is the final report for the Desert and InterMountain Air Transport project, one of five projects conducted by Southern California Edison. This project contributes to the Energy-Related Environmental Research program.

For more information on the PIER Program, please visit the Commission's Web site at: <http://www.energy.ca.gov/research/index.html> or contact the Commission's Publications Unit at 916-654-5200.

Executive Summary

The Desert and InterMountain Air Transport Project (DMAT) was approved for funding in late 1997 as a California Energy Commission (CEC) Public Interest Energy Research (PIER) Program transition program. The PIER funding allowed the completion of an ongoing Southern California Edison (SCE) environmental improvement program that had been underway since 1989 with funding from the California Public Utilities Commission and other co-sponsors. The goal of the PIER DMAT Program was to carry out fundamental research to characterize, quantify, and assess the fate and transport of air emissions and their impact on visibility from electric utility sources located principally in California to locations within California and beyond its borders. The by-products of this research have provided fundamental scientific and technical information useful to decision-makers in debating national and California visibility issues. Applying the best science available and applicable to California ensures that regulatory decisions are well founded. This report summarizes the research studies that were completed as part of the PIER DMAT Project.

The PIER DMAT Project was divided into two principal areas: completing a project on Measurements of Haze and Visual Effects (Project MOHAVE) and its supporting studies, and addressing visibility and fine particulate research issues related specifically to California.

Project MOHAVE

Project MOHAVE was designed to quantify the relative contribution of air emissions from SCE's Mohave Power Project (MPP) to visibility impairment at the Grand Canyon National Park (GCNP). Project MOHAVE was conceived in 1991 and completed in 1999 as a joint industry and government partnership involving SCE, the U.S. Environmental Protection Agency (USEPA), and the U.S. National Park Service. PIER transition funding permitted the completion of a number of Project MOHAVE research studies whose results were ultimately integrated into the Project MOHAVE Final Report.

Objectives:

- Develop new methods for judging the adequacy of regional wind fields.
- Apply an advanced reactive plume chemistry model to quantify the conversion of plume sulfur dioxide to atmospheric particulate sulfate from MPP.
- Review the optical properties of fine particulates on visual impairment and quantify the impact of MPP's emissions on visibility.
- Complete and deliver the Project MOHAVE Final Report.

Outcomes:

The PIER DMAT studies yielded information linkages important in meeting the goal of quantifying the visual impacts of emissions from MPP. For example, one of the wind fields evaluated during the PIER DMAT Project provided basic input data to the reactive plume chemistry model task. The output from the plume chemistry model task then provided information on particulate plume concentrations for various chemical constituents. These plume particulate values provided the necessary information to another PIER DMAT task to develop estimates of MPP plume impacts on visibility. These results, along with those from

other Project MOHAVE investigators, formed the content for the Project MOHAVE Final Report, the final PIER DMAT task for the Project MOHAVE research area.

Conclusions:

The key conclusion from Project MOHAVE was that there were no observational relationships linking emissions from MPP, as represented by a unique tracer, and visual impairment at locations within the GCNP. There was, however, clear observational evidence linking emissions from distant source regions such as southern and central California, northern Mexico, and nearby Las Vegas to visual impairment at the GCNP. Several different modeling methods were applied to understand the range of potential impacts from MPP. Significant differences were noted between the modeling results and are most likely due to different representations of sulfate formation chemistry in clouds assumed in each model. On average MPP was found to contribute between 0.2% to 0.6% of the total light extinction during summer at the western end of the GCNP. During “worst case” (at the 90th percentile frequency) conditions, MPP was found to contribute between 1.3% and 2.8% of the total. These levels of impact are not perceptible to the human eye.

Recommendations:

- Further research to increase knowledge of the three-dimensional patterns of wind speed and direction, as well as to gather information about the rate of formation of sulfur-containing particles in clouds, would decrease uncertainty in model predictions.
- This research identified the theoretical conditions that justify regression apportionment of light scattering, and showed how deviations from these conditions caused errors in the apportionment. It examined the degree to which these conditions were satisfied for one set of data from one location and season, but did not address how generally these results apply to other situations. Further application of this method to other settings is needed to establish whether the observations noted here are representative.
- Further work is necessary to understand the uncertainties of the Tracer Potential method for comparing wind fields.
- In performing complex plume chemistry simulations, it is extremely important to have available measurements of pollutant concentrations at plume heights consisting of ozone, nitrogen oxides, hydrogen peroxide, OH radical, water vapor, ammonia, and trace metals such as manganese and iron.
- To the extent possible within resource constraints, emission source attribution projects need to strive for hourly averaged air quality concentration data.

California-Specific Visibility and Particulate Research

The second component of the PIER DMAT Project examined a number of visibility issues relevant to California. This research area contained three sub-parts. One study examined the historical trends in emissions, visibility, and fine particulates at locations in California, including several visibility-protected national parks and monuments, to assess the extent of visual impairment in California.

Two additional efforts were coordinated under the direction of the Electric Power Research Institute. Several fundamental research activities were conducted to examine, characterize,

compare, and estimate potential errors of various methods for the measurement of fine particulate matter and its chemical components. These activities included analyses of particulate measurement programs at Riverside and Bakersfield, California.

Finally, a new and advanced air quality model was developed, which can be used to simulate the formation of atmospheric aerosols and photochemical ozone from point sources such as power plants. This model has undergone preliminary testing but additional work needs to be done before the model can be applied on an operational basis.

Objectives:

- Document the historical trends in atmospheric particulates, visibility, and visibility-impairing emissions in California.
- Relate these trends to emission trends from the energy sector in California.
- Compile a database consisting of the air quality/emission trend data.
- Evaluate the efficacy of the present generation of mathematical models for use in performing regional visibility assessments in California.
- Provide recommendations for improving the state-of-the-science for sampling PM₁₀ and PM_{2.5}.
- Develop and test an advanced point-source reactive chemistry dispersion model incorporating all of the best features (gas- and aqueous-phase chemistry, plume dynamics, aerosol dynamics, etc.) of existing models.
- Investigate the extent to which PM_{2.5} measurements made with Teflon filter-based samplers differ in mass and chemical composition from aerosol particles at the point of sampling or inhalation.
- Test, compare, and quantify the sampling errors associated with several continuous and discrete samplers designed to quantify PM_{2.5} mass or chemical composition.
- Compile onto a compact disc the Winhaze visual air quality modeler image software program and base images for several national parks in the United States, including the GCNP and Yosemite National Park in California.

Outcomes:

The objectives for all tasks were met. Specifically:

- Emissions, optical and particulate matter data were acquired and compiled into databases for subsequent analysis. The California Air Resources Board (1998) estimated annual average daily emissions of PM₁₀, nitrogen oxides, sulfur oxides, carbon monoxide and volatile organic compounds at five-year intervals from 1985 through 2010, categorized by standard industrial classification code and source category code within each county and air basin.
- Several studies were completed to identify the state-of-the-science regional modeling techniques that may be useful for particulate and visibility modeling in California. Also, a review was completed identifying potential improvements to the monitoring of fine particulates (PM_{2.5}).

- The Second-order Closure Integrated Puff model with Chemistry (SCICHEM) development was completed, which simulates liquid-phase chemistry and gas-particle thermodynamic equilibrium. Existing modules for aqueous-phase chemistry and aerosol thermodynamics were compared and the most appropriate modules incorporated into SCICHEM. The enhanced model was then tested for a range of conditions to determine if model results were physically and chemically consistent. The results from these sensitivity studies showed that the model responded in a physically and chemically consistent and directionally correct manner to all the input parameter variations.

Conclusions:

- Statistically significant decreases in concentrations occurred between 1989 and 1996 in several air basins. Most notable were decreases in the San Joaquin Valley during winter and at San Geronio Wilderness Area during spring, which are the times of year when concentrations are highest at these locations.
- Estimated emissions of PM_{2.5}, nitrogen oxides, and sulfur oxides decreased throughout the state between 1990 and 1995. These decreases are consistent with the observed decreases in concentrations. However, decreases in concentrations did not accompany decreases in emissions everywhere.
- Coupled with the decreasing trends in particulate concentrations and particulate-causing emissions, improving trends in visibility were noted in several visibility-protected areas of California including: Redwood National Park, Yosemite National Park, Point Reyes National Seashore, Pinnacles National Monument, and San Geronio Wilderness Area.
- Emissions from energy production are small percentages of PM_{2.5}, nitrogen oxide, and sulfur oxide emissions in California, so energy production likely does not contribute substantially to decreased visibility or increased PM_{2.5} concentrations.
- Emissions from non-mobile source energy use are a larger percentage of total emissions than emissions from energy production. In particular, wood burning is a substantial contributor to PM_{2.5} emissions in cooler locations, such as the Lake Tahoe and Mountain Counties Air Basins. Therefore, emissions from non-mobile source energy use may be important contributors to reduced visibility and increased PM_{2.5} concentrations in some parts of the state.
- The highest fine particle concentrations in California are present in locations with surrounding topography that limits dispersion. These areas include the Central Valley, the South Coast Air Basin, the San Francisco Bay area, and the Lake Tahoe Air Basin. The highest concentrations at these locations generally occur during the fall or winter, when periods of low inversions and low wind speeds lead to the accumulation of emitted particulate matter.
- Carbon-containing materials and ammonium nitrate are the major constituents of PM_{2.5} at the locations with the highest PM_{2.5} mass concentrations. Wood burning may be a major source of the carbon-containing materials, particularly at locations with cooler fall and winter temperatures, while the ammonium nitrate is formed from atmospheric reactions that involve nitrogen oxides and ammonia.

- Our results indicate that USEPA's Federal Reference Method for PM_{2.5} sampling does have significant limitations. It cannot assess the chemical composition of the collected aerosol, and it may be susceptible to sampling errors based on gas-particle partitioning of volatile organics and nitrate under certain conditions.
- Revision of our understanding of the composition of PM_{2.5} has additional implications beyond accurate sampling of airborne aerosol mass. Because the various components of PM_{2.5} have different dominant sources, accurate characterization of aerosol composition is necessary to design effective emission management strategies.
- The SCICHEM plume model is potentially an important tool for examining potential impacts on air quality from existing and proposed emission sources such as power plants.

Recommendations:

- More effort needs to be employed in testing the SCICHEM model against actual field measurements to provide real-world tests of model performance.
- More extensive spatial coverage is needed to better understand the nature and causes of visibility and particulate matter concentrations in California. Implementation of the PM_{2.5} monitoring network in conjunction with expansion of the Interagency Monitoring of Protected Visual Environments (IMPROVE) network will help provide this information in the future.
- Our observations highlight the need for a more robust sampling system for carbon in airborne particles that measures the gas-particle partitioning as it exists in an unperturbed air parcel.

Abstract

Relationships between air emissions, airborne particulates, and visibility were examined through a series of research projects involving particulate and meteorological measurements, plume aerosol modeling, and historical trend analyses. Two principal research areas were pursued: completing Project MOHAVE (Measurements of Haze and Visual Effects) and initiating California-specific particulate and visibility research. Project MOHAVE was initiated in 1991 as part of a U.S. Congressional appropriation to the U.S. Environmental Protection Agency to study the relative effects of air emissions from the Mohave Power Project (MPP), a large coal-fired power plant located near Las Vegas, NV, on visibility levels at the Grand Canyon National Park. Using a variety of analysis techniques, two principal conclusions were derived for the Project MOHAVE research: 1) from observational data, analysts were unable to find any statistical relationships linking emissions from MPP and visual impairment at locations within the Grand Canyon National Park; and 2) using several plume models, MPP was found, on average, to contribute during summer between 0.2 to 0.6% of the total light extinction and during worst-case conditions (90th percentile frequency) between 1.3 to 2.8% of the total. These percentage contributions are not perceptible to the human eye.

A second research area investigated the extent of visual impairment in California. This involved examining historical trends of emission-causing pollutants and visibility at several locations in California, evaluating the accuracy of particulate matter measurement methods, and developing new tools for examining plume impacts from point sources. Several conclusions were drawn from this work. The trend analysis showed that from 1989 to 1996, statewide trends in particulate concentrations exhibited statistically significant decreases in many air basins consistent with decreasing trends in emissions of oxides of nitrogen and sulfur, and volatile organic compounds. Improving trends in visibility were noted in several visibility-protected areas such as Yosemite National Park, Pinnacles National Monument, Redwood National Park, Point Reyes National Seashore, and San Geronio Wilderness Area. The particulate measurement studies found that the Federal Reference Method for measuring fine particulate matter has significant technical limitations stemming from sampling errors relating to gas-particle partitioning of volatile organics and nitrates. This finding is significant because such sampling errors may lead to underestimation of PM_{2.5} concentrations and to an improper identification of the sources of airborne particulate matter in designing effective emission management control strategies. Finally, a new state-of-the-art air quality model was developed and tested that embodies current scientific thinking regarding dispersion and chemistry of point source emission plumes. Such a model can provide a useful tool for evaluating potential impacts from new and existing power plant emissions on air quality.

1.0 Introduction

1.1 CEC's PIER Program and the DMAT Project

The California Energy Commission awarded Public Interest Energy Research (PIER) transition funding to electric utilities in December 1997 to allow completion of ongoing research that could be irreparably lost or damaged as a result of the adoption of AB 1890. The Desert and InterMountain Air Transport Project (DMAT) was approved for funding under the PIER Program having met the criteria for the Environmental Enhancement Area as a transition project. Under this funding mechanism, the PIER transition funding provided for the completion of a number of research studies previously begun as part of an existing environmental improvement air quality research program at the Southern California Edison Company (SCE). This existing SCE research program had been underway since 1989 with funding provided by the California Public Utilities Commission (CPUC) and other co-sponsors including the US Environmental Protection Agency (USEPA), Electric Power Research Institute (EPRI), the California Air Resources Board, and the U.S. National Park Service (USNPS). Two specific research areas were identified as part of the PIER DMAT research project:

- Completion of Project MOHAVE (Measurements of Haze and Visual Effects) and supporting research studies, and
- California-specific visibility and particulate research.

Each of these areas is described in more detail in this section and in other sections of this report.

In the report that follows, the specific technical work products prepared under this PIER DMAT Project contract are summarized by task number. To provide a proper continuity for the reader, references are also made to companion studies funded and completed by other sources associated with the existing SCE research program. This provides the reader with the context for the objectives developed for the PIER DMAT Project. The complete work products prepared under the PIER DMAT Project contract are contained in a series of contractor reports that are provided as the appendices to this report.

1.2 PIER DMAT Purpose and Key Objectives

The PIER DMAT Project was formulated to complete an on-going SCE research program whose purpose was to create credible scientific information to inform decision-makers as they contemplate and implement new visibility regulations resulting from the federal Clean Air Act (CAA) visibility provisions. Although visibility regulations have been a part of the CAA for almost 20 years, tackling the complexities involved with the relevant physical, chemical, optical, and human perception processes associated with visibility has been a daunting problem. The overarching goal of the PIER DMAT Project was to add relevant information to the scientific knowledge base on visibility, ultimately leading to ways to improve the quality of the air we breathe (and see).

Project MOHAVE

The on-going SCE research program, which had been underway since 1989, included Project MOHAVE, a joint governmental/industry research study. Completion of Project MOHAVE and supporting studies was a primary focus of the PIER DMAT Project. Project MOHAVE was a research study authorized by the U.S. Congress in 1991 to quantify the relative contribution of

emissions from SCE's Mohave Power Project (MPP) located at Laughlin, NV to visual impairment in the Grand Canyon National Park (GCNP). Extensive air quality, emission, and meteorological information were collected during the course of Project MOHAVE. Many new and innovative assessment methods were developed and tested. The primary objectives of this research were:

- Develop a method using the MPP tracer data to evaluate and compare the relative accuracy of predicted wind fields generated as part of Project MOHAVE. Evaluate the method, including its assumptions, sensitivity, and uncertainties. Apply it to wind fields generated from field measurements and several atmospheric models during Project MOHAVE.
- Apply the Reactive and Optics Model of Emissions (ROME) reactive plume model to simulate the atmospheric chemical dynamics in converting SO₂ emissions from the MPP plume to atmospheric particulate sulfate. Examine its sensitivity to changes in key model input parameters.
- Quantify the change in atmospheric particulate sulfate due to changes in SO₂ emissions from MPP.
- Using a Mie theory model, estimate the contributions to light extinction that would result from each of the measured particulate chemical species under a variety of assumptions about the state and properties of the aerosol.
- Calculate the effect of the modeled SO₂ emissions reductions at MPP on light extinction at Meadview under several assumptions about the growth mechanism of the secondary sulfate particles.
- Determine conditions under which light scattering budgets created by multiple regression are unbiased estimates of the actual light scattering budget, and identify the empirical consequences of departures from those conditions for actual regression-derived budgets.
- Assemble, compile, and integrate all of the individual pieces of research effort developed by the individual investigators and prepare a consistent and coherent final report. Deliver the Project MOHAVE Final Report after circulating a draft for independent peer review.

California-Specific Visibility and Particulate Research

In addition to the focus on Project MOHAVE, studies over the last decade have underscored the potential for southern California to contribute substantially to haze in the GCNP and other regions of the southwestern United States. For the past 20 years, environmental policy concerns with respect to national visibility regulations have focused on the GCNP because of its obvious scenic value. However, this situation will change in the near future as a result of the implementation of the 1999 USEPA Regional Haze Regulations. Virtually every national park in the nation will be put on an emission management path towards attaining the CAA-mandated goal of remedying all "man-made" visual impairment.

Visibility-protected areas in California (known by the CAA designation "Class I") are shown in Figure 1, along with Class I areas in Nevada, Arizona, and Utah. With 29 Class I areas of its own (six in southern California), and with mounting evidence that it is contributing to out-of-

state haze, the state of California has much at stake. Therefore, a whole host of new regulatory initiatives will likely be implemented addressing regional haze issues affecting existing and proposed new emission sources (plants) in California including power. The second PIER DMAT Project research area was directed at developing new modeling and measurement methods for application to California.



Figure 1. Class I Areas in California, Nevada, Utah, and Arizona
(The label "MPP" designates the location of the Mohave Power Project)

1.3 Program Management

SCE served as the principal investigator for the PIER DMAT Project. SCE was assisted in this effort by a number of contractors who provided specific research products for the DMAT Project. In this capacity, SCE established the overall direction and scope of the project and worked directly with individual contractors performing specific tasks to ensure that the project provided the greatest benefits to the environment and to the electric utility consumer. SCE also worked closely with contractors to ensure that all contractual responsibilities were met, budgets adhered to, and project deliverables provided. EPRI, under subcontract to SCE, was responsible for a number of the PIER DMAT research products.

1.4 Report Organization

This document is divided into five sections. This section provides an introduction and overview relating to the scope and content of the PIER DMAT Project. Section 2 summarizes all of the research work products developed as part of the technical task deliverables for this project.

Section 3 provides the conclusions derived from the project, along with recommendations for further research. Section 4 provides a list of acronyms and abbreviations, while Section 5 contains references. This report also provides the specific technical reports prepared as part of this project in a series of appendices.

2.0 Research Results

2.1 Approach

As indicated above, the PIER DMAT Project was comprised of two principal areas: Project MOHAVE and California-specific visibility and particulate research. The research studies were carried out under the PIER DMAT Project banner corresponding to the PIER DMAT Project tasks set forth in the Project work statement (Energy Commission PIER Project #6, Contract 500-97-012). Many of the task deliverables identified in the work statement have been previously provided to the CEC as part of periodic project progress reports. In the discussions that follow in this section, these tasks will be summarized by describing the background and objectives of the task, task deliverables, study methods, and results.

This research involved compiling and examining a number of data sets collected during the Project MOHAVE study as well as efforts allied with the California-specific visibility and particulate research studies. These efforts were comprised of statistical data analyses, technical reviews and development of computerized mathematical models, and comparative evaluations of alternative pollutant sampling methods and characteristics.

It should be noted that the PIER DMAT Project enjoyed the advantages of leveraging the substantial investments made by other groups as part of Project MOHAVE, as well as leveraged funding opportunities provided by the Electric Power Research Institute as part of their base budget funding for some of the California-specific visibility and particulate research studies.

2.2 Project MOHAVE

2.2.1 Background and Objectives of Project MOHAVE

Prior to summarizing the specific PIER DMAT Project results, a brief history of Project MOHAVE is provided below. In 1991, as part of a U.S. Congressional appropriation bill, the U.S. Congress appropriated \$2.5 million to the USEPA to “perform a tracer study at the Mohave Power Plant” (another name for the Mohave Power Project). The MPP is a 1580-Megawatt coal-fired power plant operated by SCE. It is located in Laughlin, NV about 90 miles southeast of Las Vegas, NV. The location of MPP in relation to a number of Class I visibility-protected areas in California, Nevada, Utah, and Arizona was previously shown in Figure 1 above.

The impetus for this study was the belief that MPP was a major contributor to visibility impairment at the GCNP. This belief was formed as a result of several studies performed by the USNPS in the 1980’s that examined regional sources of emissions estimated to cause visual impairment at the GCNP (Gebhart et al. (1988 and 1993), Malm (1989), and Latimer (1991)). Other emission source regions also thought to contribute to regional visibility impairment included southern California, the Navajo Generating Station located in northern Arizona, and several large copper smelters located in southern Arizona and New Mexico.

Other studies by SCE (Murray, et al., 1990), though, also examined the effects of MPP during a six-month shutdown in the latter half of 1985. These studies looked at the distribution of particulate sulfate concentrations, a major contributor to haze in the southwest. They found that during the time period of the MPP shutdown, compared to other time periods at the GCNP,

As a consequence of these conflicting sets of analysis results, Project MOHAVE was initiated. The primary goal of Project MOHAVE was to determine the contribution of the MPP emissions to haze at the GCNP and other nearby mandatory Class I areas where visibility is an important air-quality-related value. This included a quantitative evaluation of the intensity, spatial extent, frequency, duration, and perceptibility of the MPP contribution. The improvement in visibility that would result from the control of MPP emissions was part of this primary goal.

The actual field data collection portion of the project was carried out in 1992 in the southwestern United States with the completion of two intensive monitoring periods, one in the winter of 1992 and the other during the summer of 1992. A reduced level of effort monitoring program was also carried out from February 1992 to July 1992. Extensive air quality and meteorological measurements were collected during the project. A detailed discussion of the data collected and their analyses can be found in the Project MOHAVE Final Report (Pitchford, et al., 1999), the executive summary of which is included as Appendix A of this document. The location of the air quality sites is provided in Figure 2.



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- El Centro, CA to document transport from northern Mexico,
- Tehachapi Mountains to document transport from the southern San Joaquin Valley of California, and
- Dangling Rope, Arizona to document the impacts of emissions to the east of the GCNP.

Several different types of analyses were carried out during the project. These analyses included examining the relationships between various measurements such as MPP tracer and particulate and light extinction levels at various study monitoring locations, and applying mathematical models to apportion particulate sulfur and visibility impairment to emission source areas including MPP. Appendix B contains analytical data pertinent to a significant finding resulting from the research: a lack of correlation between MPP tracer, elevated levels of sulfates, and visibility impairment at the GCNP.

During the course of the Project MOHAVE data analysis efforts, a number of knowledge gaps were identified, dealing with the treatment of plume chemistry in the various assessment models being applied. These knowledge gaps were addressed by the research tasks undertaken in the PIER DMAT Project.

The Project MOHAVE Final Report was completed and submitted to the USEPA on March 19, 1999. Table 1 provides a listing of the various investigators who contributed to Project MOHAVE. The interested reader can obtain the Final Report by visiting the USEPA Internet site at <http://www.epa.gov/region09/air>.

Table 1. Contributors to Project MOHAVE

U.S. Environmental Protection Agency	Southern California Edison Company
U.S. National Park Service	Electric Power Research Institute
National Oceanographic and Atmospheric Administration	California Energy Commission
California Resources Board	Washington University
ENSR Corporation	California Public Utilities Commission
University of Southern California	University of California – Davis
Atmospheric and Environmental Research, Inc.	Brigham Young University
Yamada Arts & Science Corp	Dr. Ivar Tombach – Environmental Consultant
Harvard University	Colorado State University
University of Minnesota	Brookhaven National Laboratory
Technical & Business Systems	Desert Research Institute
MPP Co-Owners (Los Angeles Department of Water & Power, Salt River Project, and Nevada Power Corp.)	Air Resource Specialists

2.2.2 Project MOHAVE/PIER DMAT Timeline

The total time period for Project MOHAVE spanned from its original U.S. Congressional appropriation in 1991 until its formal completion in 1999 with the publishing of the Project MOHAVE Final Report to the USEPA. Because of the substantial amounts of data collected by

at least 20 different investigators of Project MOHAVE, significant amounts of time were devoted to collection, quality checking, databasing, and analyzing these data. An initial round of model evaluations for simulating the MPP tracer took place in early 1996. The evaluations resulted in the conclusion that none of the model performances were deemed adequate for use in MPP source impact determinations. This necessitated a second round of new and substantially more complex model development efforts from 1996 to 1998. All formal work on Project MOHAVE virtually ceased from 1994 to 1996 in order to address the technical needs of the Grand Canyon Visibility Transport Commission (GCVTC), which completed its final report to the USEPA in June 1996 (GCVTC, 1996). A timeline of the Project MOHAVE study efforts is shown in Table 2-2. The Energy Commission PIER efforts spanned the period from January 1998 to December 1999.

Table 2. Timeline of PIER DMAT Project/Project MOHAVE

ACTIVITY	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
US Congressional Authorization ▲										
Project MOHAVE Study Plan ●	●									
Winter Field Study ●		●								
Summer Field Study ●		●								
Data Base Development ●		—		●						
GCVTC Study ●			—			●				
Preliminary Project MOHAVE Model Evaluation ●						—	●			
Release of MPP Tracer Data ▲							▲			
Development of Refined Models ●							—	●		
Draft Final Report for Peer Review ●								●		
CEC PIER DMAT Funding								—	●	
Final Report ●								—	●	

2.2.3 Reliability of Regional Wind Fields

2.2.3.1 Background and Objectives

Note: This work was performed as PIER DMAT Task 2.1.

Objectives:

- Develop a method, using the MPP tracer data, to evaluate and compare the relative accuracy of predicted wind fields generated as part of Project MOHAVE.
- Evaluate the method, including its assumptions, sensitivity, and uncertainties.
- Apply the method to wind fields generated from field measurements and several atmospheric models during Project MOHAVE (Pitchford, *et al.*, 1999).

Deliverables:

Contractor Report: Koracin, D., J. Frye, and V. Isakov (1999). A Method of Evaluating Atmospheric Models Using Tracer Measurements. *Journal of Applied Meteorology*, accepted for publication (See Appendix C).

Background:

Realistic representations of three-dimensional atmospheric fields are essential for the simulation of the transport and diffusion of atmospheric pollutants with air quality models. A key element of the atmospheric field is the wind that transports emitted pollutants. This element is expressed in terms of the spatial and temporal distribution of the wind speed and direction over a geographical region.

The predictions by an air quality model cannot be better than the quality of the wind information used in it. This wind information is typically provided by interpolation of measurements or is generated by a wind field model. Different approaches do not always produce consistent wind fields, especially in the complex terrain of the western U.S. where MPP is located. Therefore, it would be useful to have a tool that evaluates the wind fields that are produced and provides a measure of how well each method represents reality. Figure 3 provides a topographic view of the complex terrain in the MPP site region.

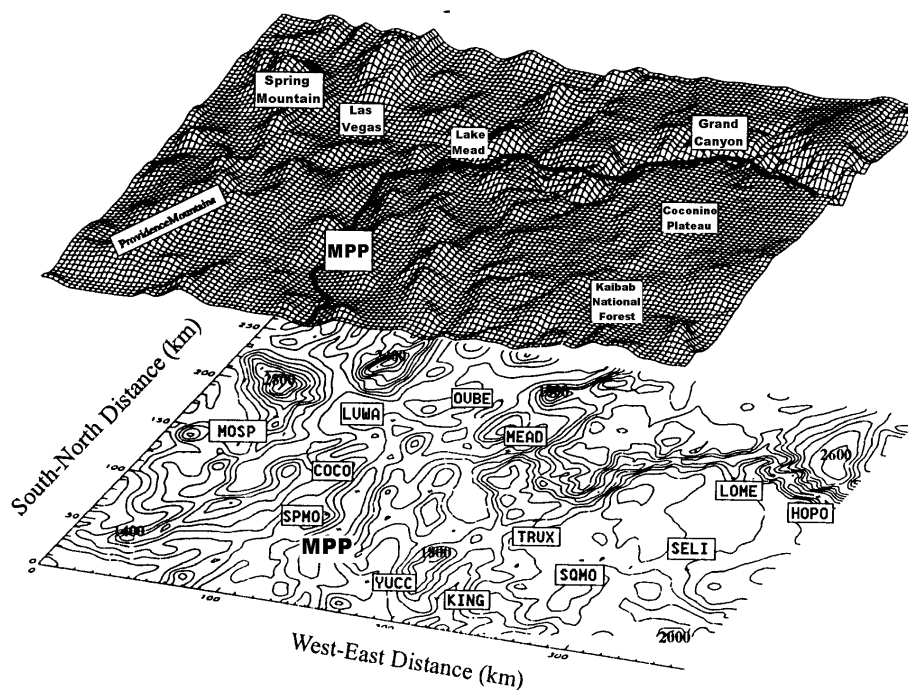


Figure 3. Topography of the Colorado River Valley.
Contour interval is 100 meters. MPP is the Mohave Power Project.

Many recent regional air quality measurement and modeling studies have included injection of a tracer material into the emissions from a source or source region. This tracer serves as a unique marker of the air mass that contains the pollutants emitted from that source. The measurement of ambient concentrations of the tracer over time and space defines where these pollutants have been transported by the wind, and how much they have been diluted by mixing into the surrounding atmosphere.

This information about the distribution of the ambient tracer concentrations can also be used to evaluate the predictions of a wind field model. Generally, this is accomplished using the wind field to construct transport trajectories from the source. The paths of these trajectories over the ground are compared with the locations of the highest tracer concentration observations. If the trajectories pass near the locations where the measured concentrations are highest, then the wind field is taken to be a good representation of the actual transport wind.

There are limitations to this approach. It is subjective and, therefore, qualitative. Consequently, it cannot be used for making an objective comparison of the qualities of two different wind fields. Furthermore, if the sampling network is sparse (and it usually is), the true peak concentration locations with which the trajectories should coincide may not be at sampling locations but rather lie between them, which leads to uncertainty in the evaluation.

These limitations inspired the need for a technique that could evaluate the quality of wind fields and assign figures of merit to them, and that would work even if the sampling network was not fine enough to discern the cross-sectional structure of the tracer plume. This need led to the research that is summarized here and is described in greater detail in Koracin *et al.* (1999) which is attached as Appendix C.

The technique evaluates only wind fields prior to incorporation of dispersion into the model calculations. The results of this evaluation cast some light on the relative accuracy of the

transport patterns as calculated by the various models in the MPP emission source attribution for visibility impairment. The most important use of this method is to select the wind fields that are best able to represent tracer transport. The method can be used as a screening tool to provide the most accurate wind fields to dispersion modelers. This application yields a solid base for improvement of dispersion models and prevents erroneous modifications of the models due to inaccurate wind fields.

2.2.3.2 Methods

The method that was developed for evaluating wind fields using tracer data relies on a function that was created for this purpose and is named the “tracer potential” (TP) function. Specifically, for a given receptor at which tracer concentrations were measured, a 3-dimensional field of tracer potential values surrounding the receptor is defined according to the formula

$$TP(x,y,z) = c/(r + r_0).$$

Here, c is the measured concentration of the tracer at the receptor and r is the distance from the receptor to any location (x,y,z) in the atmosphere. The constant r_0 is needed to keep the value of TP finite at the receptor, where $r = 0$. For convenience, we can set $r_0 = 1$, so $TP = c$ at the receptor and it decreases roughly $1/r$ as one moves away from the receptor. This field of TP values applies over the period of time that the measurements of c were made; a new TP field is generated when the next measurement is used. Since measurements of tracer concentrations are typically only available at ground-level (i.e., for $z > 0$), the TP for $z = 0$ will generally be the only one used.

When there are many receptors, each with its own measured concentration, the TP at any point in space is just the sum of the TPs attributable to each of the individual receptors. The TP field then provides a portrayal of the location of the tracer plume, because the largest values of TP occur in the area where the highest concentrations were measured.

Now, take the point (x,y,z) to be a point on a wind trajectory from the tracer source. That point represents the location of an air parcel at the same time as the tracer measurements that define the TP were made. Then, the TP value at that point can be considered as a figure of merit that expresses how closely that point on the wind trajectory coincides with the location where the measured tracer concentrations indicate the location of the plume to be. The TP has its highest value when the trajectory point is at the same location as the tracer plume location, and has a lower value further from that location. It is higher where the tracer concentrations are higher and is lower where the tracer concentrations are lower. (Although the TP field is usually only defined at the surface, $z = 0$, we can still use this same approach to evaluate wind trajectories at different levels above the ground by assuming that the transported material is mixed down to the ground at the receptor. One can also use a trajectory that reflects the integrated transport effect of winds at several levels.)

If one defines an initial TP_0 at the location of the source, then TP will either increase or decrease from this value as the air parcel is transported away from the source. (Typically, TP_0 is not a maximum, particularly for measurements made on the surface, because the plume doesn't reach the ground until some distance from the source.) For the typical measurement of tracer concentrations along the surface, it is useful to reference the values of TP relative to TP_0 , and

the discussion from here on will deal with TP values relative to this reference. Using this new reference, values of TP can be positive or negative. Values of $TP > 0$ along a trajectory tend to reflect “success” in finding the location of the measured tracer plume. Conversely, values of $TP < 0$ tend to reflect lack of success in finding the location of the plume.

Often, tracer concentrations are measured as averages over periods of many hours, while wind fields are updated hourly. For the example of a 6-hour sample, this means that there will be six points along one trajectory from the source that correspond to predicted plume air parcel locations at each of the six hours of sampling. One can then create an integrated (or “net”) TP for this trajectory over the sampling period by integrating the area under the curve of a plot of TP versus time along the trajectory (creating, in effect, an average TP for the period, multiplied by the length of the period). This integrated TP is called the TP area. There will also be six separate trajectories generated over the six-hour period, one starting at the source each hour, so the overall TP area for the sample will be the average of six of these integrated TP areas.

The value of the TP or TP area that is derived is a number that can only be interpreted in a relative sense; its magnitude has no obvious physical significance. To provide a quantitative figure of merit, it is useful to divide the TP or integrated TP area by the maximum value that it would have in the presence of a trajectory that perfectly represents the measured concentration distribution. Since this actual trajectory is not known, a numerical procedure was developed to generate the trajectory that would produce the maximum integrated TP and this highest value was taken as an approximate representation of the TP area of a perfect trajectory. The success, s , of the predicted trajectory is then defined as

$$s = TP / TP_{\max} ,$$

where TP_{\max} is the maximum TP (or TP area) that results from the synthesized approximation of a perfect trajectory. A single TP or the TP area can be used in the success formula, as appropriate, since TP area is just a composite of multiple TPs.

A value of $s < 0$ means that the predicted trajectory is a poor estimate of the actual trajectory. (Recall that TP and TP area can be less than zero, because they are calculated so that $TP = 0$ at the source.) A value near unity means that the predicted trajectory is close to the synthesized highest TP trajectory. Typical values lie between 0 and 1, and can be expressed as a percent.

2.2.3.3 Results and Discussion

The TP method was applied to evaluating the quality of six wind fields that were derived from measurements and modeling performed for the summer 1992 intensive period of Project MOHAVE (Pitchford *et al.*, 1999). Measurements made during 38 days, selected from the period from July 12 to August 31, 1992, were used for this analysis. The wind fields tested encompassed the following:

- Interpolated wind measurements from four radar profilers.
- Wind fields generated by the California Meteorological Model (CALMET). (A diagnostic model objectively interpolates measurements and applies physical constraints, such as mass conservation, to the interpolation.) Both routine meteorological observations and radar profiler measurements were used as input data.

- Wind fields generated by the Enger-Koracin (EK) higher order turbulence closure model for a set of conditions, with the field for each day selected to be that one which compared most favorably with wind profiler measurements. The EK model is a prognostic meteorological model. (A prognostic model derives the meteorological conditions from the first principles, and the equations of state and motion, starting with measured or synthesized initial and boundary conditions.)
- Wind fields generated by the Mesoscale Model Version 5 (MM5), another prognostic model, for the period from August 7 to 14, 1992.
- Wind fields generated for the period from August 6 to 16, 1992 by the Higher Order Turbulence Model for Atmospheric Circulation (HOTMAC) prognostic model. Wind profiler measurements were used for “nudging” the model’s calculations.

According to the TP analysis, the most successful of these methods was the CALMET wind field when the wind field at the most probable effective plume height was used to define the trajectories. It was the only model that yielded positive values for the TP area during the entire period. Its highest success rate, s , was 22% and s was greater than 10% on 23 of the days. The interpolated wind profiler fields had the highest single-day success rate (37%), but the results varied greatly from day to day and the TP area was negative on eight of the days. The two prognostic models, MM5 and HOTMAC, showed similar results, with success greater than 10% on several days of the short periods over which they were tested, but they also showed one or two days with negative TP area. The approximation of measured conditions with the EK wind fields had relatively low success.

If the evaluation is limited to receptors relatively close to the source, in the region where the TP values for all models tended to be positive, then CALMET, MM5, and HOTMAC all performed roughly comparably, with daily success rates up to about 20%. The average success of the interpolated wind profiler fields was not as good as that of these three models. Thus, incorporation of measurements into a diagnostic model (CALMET) appears to significantly improve the success rate over that which is obtained by simply interpolating measurements. Also, the HOTMAC wind fields that were nudged with measurements yielded success rates similar to those of the MM5 fields, which did not incorporate nudging.

This example illustrates the capability of the tracer potential method for evaluating wind fields when tracer data are available. Application of the TP method produces meaningful information concerning the performance of various wind fields. This information can be used as guidance for selecting the appropriate wind field, as well as for diagnosing means to improve the capability of a given wind field generation method.

Thus, the objectives of the research were met.

Recommendations

- Further work on understanding the uncertainties of the TP method is desirable. A question deserving attention is the sensitivity of the results to receptor spacing, especially in the case where the receptors are so far apart that the plume could pass between two of them undetected. There is clearly a receptor spacing beyond which the TP method’s results will be highly uncertain. Further refinement of the method, particularly for use with three-dimensional trajectories, should be undertaken. In

addition, if tracer measurements aloft become available, it would be desirable to test the full three-dimensional formulation of the method.

2.2.4 Chemical Characterization of the MPP Plume

2.2.4.1 Background and Objectives

Note: This work was performed as PIER DMAT Task 2.2.

Objectives:

- Apply the Reactive and Optics Model of Emissions (ROME) reactive plume model to simulate the atmospheric chemical dynamics in converting SO₂ emissions from the MPP plume to atmospheric particulate sulfate.
- Examine the sensitivity of the ROME model to changes in key model input parameters.
- Quantify the change in atmospheric particulate sulfate due to changes in SO₂ emissions from MPP.

Deliverables:

Contractor Report: Karamchandani, P., Y. Zhang, and C. Seigneur, 1998. Simulation of sulfate formation in the Mohave Power Project plume, Paper No. 98-RP101A, presented at the 91st Annual Meeting & Exhibition of the Air and Waste Management Association, June 14-18, San Diego, CA (See Appendix D).

Background:

During the course of Project MOHAVE, many different assessment models were proposed and applied to quantify the impacts of emissions from MPP. These models incorporated different techniques for treating the atmospheric chemical conversion of MPP SO₂ emissions to particulate sulfate, which was of greatest interest in this project. These techniques ranged from simple first-order constant conversion assumptions to reactive plume models incorporating advanced plume and chemical modules. Although easy to apply, the simple models lacked the scientific rigor necessary to capture the complex physical and chemical dynamics that are involved in simulating the transport and chemistry of plumes.

Therefore, a need was identified to develop, test, and apply a reactive plume modeling methodology capable of predicting the conversion of MPP SO₂ emissions to particulate sulfate and the contribution of MPP sulfate to measured sulfate at a number of locations in the Grand Canyon region. Using this methodology, it was possible to determine the contribution of MPP's emissions to particulate sulfate and hence to light extinction at locations in the GCNP. A complete description of the modeling methodology and its applications can be found in Appendix D.

2.2.4.2 Methods

The modeling method developed as part of this task was based on ROME (Seigneur et al., 1997). ROME includes state-of-the-science formulations of the governing transformation processes, including gas- and aqueous-phase reactions, gas-liquid equilibria, gas/particle equilibria, and aerosol dynamics and chemical composition. The model uses a Lagrangian or trajectory approach to simulate the transport and dispersion of the MPP plume, and simulates

the gas- and aqueous-phase reactions that occur as the plume mixes with background air. (Background air is defined as the air outside the plume). Of particular interest are the conversion of SO₂ emissions to particulate sulfate, and conversion of oxides of nitrogen emissions to particulate nitrates.

SO₂ conversion rates in a power plant plume can be significantly different from ambient background conversion rates because oxides of nitrogen (NO_x) concentrations that affect oxidant levels in the plume are significantly different in the plume vs. the background air. Plume SO₂ conversion rates are strong functions of the background chemical concentrations, plume dispersion, and interactions of the plume with fog and clouds. Furthermore, plume conversion rates vary with time because (1) the gas-phase reaction is a function of OH radical concentrations that are affected by daily photochemical activity; (2) the aqueous-phase reaction with hydrogen peroxide (H₂O₂) is typically oxidant limited in a plume and will proceed rapidly but will stop when the H₂O₂ is depleted; and (3) the aqueous-phase reactions with oxygen molecules (O₂) (catalyzed with iron (Fe) and manganese (Mn)) and ozone (O₃) are self-limiting because their rates decrease with decreasing pH. In addition, the aqueous-phase conversion processes lead to non-linear relationships between SO₂ and sulfate. Such non-linear relationships cannot be simulated with constant conversion rates such as were used in other Project MOHAVE models. Thus, it was necessary to simulate these chemical processes explicitly to properly represent the conversion of SO₂ to particulate sulfate in the MPP plume. The approach adopted in this study was to use a reactive plume model with a detailed treatment of the gas-phase, particulate-phase, and droplet-phase chemical reactions that govern the conversion of SO₂ to particulate sulfates.

The ROME model consists of a two-dimensional array of contiguous grid cells that is perpendicular to the mean wind direction. These cells can expand horizontally according to a Gaussian distribution for inert species. The vertical depths of the cells remain constant during a given model simulation. Reactive chemical species undergo chemical reactions in and between the cells and background according to a Fickian diffusion algorithm. Concentrations of emitted species that are considered inert are assumed to follow a Gaussian distribution. In addition, vertical diffusion and convection occur for all species (inert and reactive), since the vertical grid structure of the model does not change during a given simulation. A variety of options are available to specify or calculate horizontal and vertical dispersion coefficients, and the model includes a state-of-the-science formulation for plume rise and dispersion using second-order closure algorithms.

ROME also includes modules for gas- and aqueous-phase chemistries and gas-liquid equilibria, aerosol dynamics and chemical composition, dry and wet deposition, and atmospheric optics. The gas-phase chemistry of volatile organic compounds (VOCs), NO_x, and photochemical oxidants is based on the most recent version of the Carbon Bond Mechanism IV (CBM IV), (Gery et al., 1989 with subsequent revisions). The gas-phase oxidation of SO₂ is simulated using the kinetic expression of Atkinson and Lloyd (1984).

In the presence of clouds, the aqueous-phase chemistry module of ROME is activated. Cloud water content can either be prescribed as an input or can be calculated internally in the model using a cloud microphysics module. The aqueous-phase chemistry module includes 30 irreversible reactions, 13 ionic equilibria, and 18 gas-liquid equilibria (Seigneur and Saxena,

1988). Three major pathways leading to SO₂ oxidation in the aqueous-phase are included in the mechanism. These include oxidation by H₂O₂, O₃, and O₂ (catalyzed by Fe and Mn). The oxidation of SO₂ by H₂O₂ has been shown to be very rapid (Hoffman and Calvert, 1985), and SO₂ and H₂O₂ typically do not coexist in atmospheric clouds unless SO₂ is complexed as hydromethanesulfonic acid by formaldehyde. The aqueous-phase chemical mechanism in ROME simulates this titration of SO₂ by H₂O₂. The oxidation reactions of SO₂ with O₃ and O₂ are slower and have chemical kinetics that depend on the pH of the cloud's droplets (Hoffman and Calvert, 1985; Martin, 1984). ROME uses the most recently available laboratory data to simulate these reactions.

Gabruk (1999) and Seigneur (1999) have previously undertaken evaluations of the various modules of the ROME model, using a variety of different field data. The CBM IV chemical mechanism, in addition, has undergone a number of extensive evaluations and improvements by the USEPA since the CBM IV was implemented in the USEPA Urban Airshed Model, the approved model for urban airshed photochemical applications.

ROME requires meteorological and dispersion data, as well as background chemical concentration data along the plume trajectory, to perform the transport, dispersion, and chemistry calculations. In addition, MPP emissions of oxides of sulfur (SO_x), NO_x, tracer, and trace metals such as iron and manganese are also required to specify the initial concentrations in the plume near the stack. The stack emissions data were obtained from stack tests conducted during the Project MOHAVE intensive monitoring periods.

The meteorological data required by ROME consist of plume wind speeds or travel times as well as vertical profiles of temperature, air pressure, relative humidity, and cloud liquid water content. The dispersion data consist of plume widths and vertical profiles of eddy diffusion coefficients along the plume trajectory. The meteorological input data were derived from the results of Lu and Yamada (1998), who applied a three-dimensional mesoscale meteorological modeling system and a three-dimensional Lagrangian random puff dispersion model to simulate the wind, turbulence, and tracer gas concentrations observed during the summer intensive monitoring period of Project MOHAVE. The model employed was previously evaluated using the method developed by Koracin (1999) in PIER DMAT Task 2.1 (see Section 2.2.3).

The background chemistry data include concentrations of O₃, NO_x, H₂O₂, VOCs, peroxyacetyl nitrate (PAN), carbon monoxide (CO), ammonium (NH₃), and tracer metals such as iron and manganese. Wherever possible, these data were obtained from ground-level and aircraft measurements conducted as part of the summer intensive monitoring period of Project MOHAVE. For chemicals that were not monitored, a literature survey was carried out to estimate representative concentration values.

2.2.4.3 Results and Discussion

A number of trajectories were simulated covering an 11-day period from August 6 to August 16, 1992. These trajectories originated at MPP and generally moved in the direction of Meadview at the western end of the GCNP. The trajectories were selected during time periods when the MPP tracer concentrations were highest at Meadview during this period. After the trajectories were selected, initial and background chemistry conditions and meteorological

input data required for the ROME simulations were developed. Transport/chemistry calculations were then performed for these trajectories.

Tables 3 and 4 summarize the results for the Meadview and Hopi Point monitoring sites. These tables show model estimates of sulfate concentrations attributable to MPP that were calculated for each 12-hour averaging period from trajectories that were simulated for Meadview and Hopi Point. The measured 12-hour average sulfate concentrations for each period and the relative contribution of MPP to the measured sulfate are also provided. In addition, an aggregate MPP sulfate to MPP SO₂ ratio is an approximate measure of the conversion of MPP SO₂ to sulfate.

Table 3. Transport/Chemistry Results for Meadview, ROME Model

Date of Initial Time	12-hr Period	MPP Sulfate (ng/m ³)	Sulfate (%) SO ₂	Observed Sulfate (ng/m ³)	Calculated MPP Contribution to Sulfate (%)
8/5/92	7pm – 7am	22	1	1636	1.3
8/6/92	7am – 7pm	123	18	2673	4.6
8/6/92	7pm – 7am	31	3	2918	1.1
8/8/92	7pm – 7am	8	<1	1645	<1.0
8/9/92	7am – 7pm	90	5	2043	4.4
8/13/92	7am – 7pm	10	3	1347	<1.0
8/13/92	7pm – 7am	92	2	1791	5.1
8/14/92	7am – 7pm	244	14	2891	8.4
8/14/92	7pm – 7am	382	30	2037	18.8
8/15/92	7pm – 7am	190	13	2514	7.5
8/16/92	7am – 7pm	53	8	2437	2.2

Table 4. Transport/Chemistry Results for Hopi Point, ROME Model

Date of Initial Time	12-hr Period	MPP Sulfate (ng/m ³)	Sulfate (%) SO ₂	Observed Sulfate (ng/m ³)	Calculated MPP Contribution to Sulfate (%)
8/6/92	7pm – 7am	2	13	1217	<1.0
8/7/92	7am – 7pm	17	15	1799	<1.0
8/9/92	7am – 7pm	96	37	1572	6.0
8/9/92	7pm – 7am	28	39	1648	1.7
8/15/92	7pm – 7am	64	37	1322	4.8
8/16/92	7am – 7pm	129	29	2014	6.4

As shown in these tables, the following results were obtained:

- Estimated contribution of MPP to 12-hour average sulfate concentrations measured at Meadview ranged from less than 1% to 18.8% for these simulations.
- Over the entire period, the estimated average MPP contribution to 12-hour average sulfate concentrations was about 5%.
- The MPP sulfate to MPP SO₂ ratio ranged from less than 1% to 30%. The average ratio over the period was about 9%.
- At Hopi Point, MPP sulfate concentrations were smaller than those at Meadview. The estimated MPP contribution to observed 12-hour average sulfate ranged from less than 1% to 6%.
- The MPP plume had significant interactions with clouds during only one time period (the night of August 5, 1992) as it traveled to Meadview. These trajectories were fast-moving and had short residence times and impact times at Meadview. None of the trajectories from MPP to Hopi Point encountered clouds at plume levels.

Several other model cases were also examined to assess the sensitivity of the modeling calculations and results to changes in the input data. The following results were obtained:

- Changing the background concentrations to enhance sulfate formation in the plume (e.g., increasing VOC, O₃, PAN, Fe, Mn, and NH₃ and decreasing background SO₂ concentrations) did not always result in higher sulfate concentrations, because the long travel times of the plume led to various chemical regimes.
- As expected, increasing the interaction of puff trajectories with clouds increased the conversion of SO₂ to sulfate in the plume. This effect is enhanced when the H₂O₂ available for aqueous-phase oxidation is implicitly increased by setting background levels of SO₂ to zero. For an extreme hypothetical scenario, the upper bound value for the MPP sulfate contribution for a cloudy day was 18%.

Finally, a model simulation was performed to determine the change in MPP sulfate concentrations at Meadview for a 90% change in MPP SO₂ emissions. The overall reduction in MPP sulfate found for two selected puffs was an 81% reduction, a slightly non-linear response.

The objectives of this task were met.

2.2.5 Contribution of Sulfate to Light Extinction

2.2.5.1 Background and Objectives

Note: This work was performed as PIER DMAT Task 2.3.

Objectives:

- Using a Mie theory model, estimate the contributions to light extinction that would result from each of the measured particulate chemical species under a variety of assumptions about the state and properties of the aerosol.
- Calculate the effect of the modeled SO₂ emissions reductions at MPP on light extinction at Meadview under several assumptions about the growth mechanism of the secondary sulfate particles.

Deliverables:

- Contractor Report: Lowenthal, D.H., J.G. Watson, and P. Saxena (1999). Contributions to Light Extinction during Project MOHAVE. Submitted to *Atmospheric Environment* (See Appendix E).

Background:

Using the extensive air monitoring data collected during the summer 1992 Project MOHAVE field study, the contribution of aerosols to light extinction at the Meadview site was estimated using Mie theory and size-resolved aerosol chemical measurements. Of particular interest was the contribution of size-resolved sulfate particulates to light extinction, which has been shown from the Project MOHAVE measurements to contribute an average of 18-20% of the total light extinction in the GCNP.

This research provided information for relating the measured aerosol concentrations and the results of the sulfate modeling studies to the light extinction at Meadview, AZ (near the western end of GCNP). The calculation of the optical effects of the aerosol requires information about the aerosol that is not readily measurable, and therefore assumptions have to be made about the state of the aerosol and some of its properties. It is important to understand how these assumptions affect the conclusions that are reached.

The methods and findings of this research are summarized here. It is described in greater detail in Appendix E.

2.2.5.2 Methods

Particle light extinction was calculated by applying a Mie theory model, Elastic Light Scattering Interacting Efficiencies (ELSIE) (Sloane, 1986; Lowenthal *et al.*, 1995), to the speciated aerosol composition measured by the Interagency Monitoring of Protected Visual Environments (IMPROVE) sampler at Meadview during the summer 1992 intensive study of Project

MOHAVE. Mie theory defines the light scattered and absorbed by a spherical particle of specified size and index of refraction. The contributions of sulfate, nitrate, organic carbon (OC), elemental carbon (EC), and soil dust particles were calculated. The size distributions of all species except nitrate were determined from measurements made by Micro Orifice Uniform Deposit Impactor (MOUDI) size fractionating impactors at Meadview; the nitrate size distribution, which was not measured, was assumed to be the same as that of sulfate.

Several aspects of the aerosol were not known, and so the Mie theory modeling was used to test alternative assumptions about its makeup. Specifically, it was not known whether the fine particles were internally mixed (i.e., every particle in the aerosol is a mixture of the various chemical species and has the same relative chemical composition) or externally mixed (the aerosol consists of separate particles of sulfate, nitrate, organic carbon, etc.), so calculations were made for both mixing states. In addition, the effects of two alternative assumptions about the degree of neutralization of the sulfate were tested. Also tested were the effects of assumptions about several unknown properties of the organic carbon particles at Meadview, including their hygroscopicity (i.e., the affinity of the OC particles for water), their carbon fraction, their density, and their refractive index.

These results were compared with measurements of light scattering and absorption.

Mie theory was also used to determine the scattering efficiency of each species. The scattering efficiency for a species is the change in light scattering associated with a unit change in the concentration of that species. Each scattering efficiency was calculated from the change in light extinction that was associated with a small decrease in the concentration of the respective species. These scattering efficiencies were then multiplied by the measured species concentrations to construct light extinction budgets, which apportioned the total light extinction to the various species.

The final analysis of the research was a calculation of the effect of a decrease in ambient sulfate concentrations, due to a removal of MPP emissions, on light extinction at Meadview. One of the modeling systems used during Project MOHAVE encompassed the HOTMAC meteorological model, the Random Puff Transport and Diffusion Model (RAPTAD), and the ROME plume chemistry model. Analyses with this system, the most sophisticated modeling system applied during Project MOHAVE, during part of the summer 1992 period indicated that the largest 12-hour average contribution of MPP emissions to sulfate at Meadview was 19% of the measured sulfate concentration. In the research program described here, the light extinction impact of this level of decrease in sulfate was calculated by Mie theory, under four different assumptions concerning the effect of this removal on the size distribution of the sulfate particles.

2.2.5.3 Results and Discussion

The Mie theory calculations of light scattering yielded results that average absolute errors within 13.8% to 22.7% of the values measured by a fine particle integrating nephelometer (a device that continuously measures light scattering) at Meadview. The estimates were largely insensitive to assumptions about sulfate neutralization, aerosol mixing state, and OC hygroscopic properties. The largest deviations from the measured light scattering (those with average absolute errors greater than 18%) were associated with relatively non-conventional

assumptions about the fraction of carbon in organic particles and the density of OC particles. Better results were obtained by multiplying the measured OC mass by 1.2 to obtain the mass of organic particles and using a specific gravity of 1.2 for those particles, than by using other values.

The Mie theory calculations produced light absorption coefficients that were much smaller, by factors of 7 to 12, than those derived from measurements made by the laser integrating plate method (LIPM). This discrepancy appears to be due to a systematic error in the LIPM measurements. This conclusion is supported by analyses of the integrating plate method by Horvath (1997a, 1997b), who concluded that the method significantly overestimates light absorption for aerosols in which only a minor portion of the light extinction is due to absorption, as is the case for the Meadview data.

The extinction budgets indicated that, on average, Rayleigh scattering by air molecules accounted for 39.4% of the light extinction at Meadview in the summer of 1992, coarse particles accounted for 21.2%, sulfate-containing particles for 19.4%, and organic carbon particles for 8.6%. Fine particle absorption was estimated to account for 4.6%. The extinction thus calculated was considerably lower than the extinction measured by a transmissometer, however, this discrepancy has not been explained.

Calculations of the effect of the removal of MPP emissions found that a 19% decrease in ambient sulfate would produce a decrease in light extinction of between 3.3% and 5.3%, depending on the assumed effect on the sulfate size distribution.

The sulfate formation process that produced the 19% estimate in the model involves gas-phase surface reactions of SO₂ on existing particles. Mie theory calculations based on the size distribution effects of this process indicate that the dry extinction efficiency of the removed sulfate is in the vicinity of 2 m²/g. This value is considerably smaller than the value of 3 m²/g that is typically used to represent sulfates. The higher value was found here to be associated with liquid-phase volume reactions of SO₂ in droplets. Based on these analyses, Project MOHAVE used 2 m²/g as the extinction efficiency of MPP sulfate when calculating the contribution of MPP emissions to GCNP light extinction.

The objectives of this task were met.

2.2.6 Reconciliation of Scientific Issues Regarding Light Extinction at the Grand Canyon

Note: This work was performed as PIER DMAT Task 2.4.

Objectives:

- Assemble, compile, and integrate all of the individual pieces of research effort developed by the individual investigators and prepare a consistent and coherent final report.

Deliverables:

- Various scientific reports from the numerous study investigators were integrated into the Project MOHAVE Final Report.

Background:

The Project MOHAVE Final Report was prepared by a number of investigators in several organizations, with each investigator preparing their own section of the report. The objective of this task was for a single investigator to work with the various contributors to Project MOHAVE in finalizing the report. Under this task, this single investigator accumulated all of the report sections, assembled them into a single comprehensive report, provided consistency in terms of style, and edited the resulting report for review. This investigator was also responsible for collecting the comments from the independent peer review scientists and ensuring that all of their comments were addressed. This particular task was undertaken and successfully completed by Dr. Ivar Tombach, private consultant.

The objective of this task was met.

2.2.7 Light Extinction Estimation and Measurements

Note: This work was performed as PIER DMAT Task 2.5.

2.2.7.1 Background and Objectives**Objectives:**

- Determine conditions under which light scattering budgets created by multiple regression are unbiased estimates of the actual light scattering budget. Identify the empirical consequences of departures from those conditions for actual regression-derived budgets.

Deliverables:

- Contractor Report: Vasconcelos, L. A. de P., Macias, E. S., McMurry, P. H., Turpin, B. J. and W. White, 1999. A Closure Study of Extinction Apportionment by Multiple Regression. Submitted for publication to *Atmospheric Environment*, August (See Appendix F).

Background:

Both federal USEPA and regional/state air quality regulators are considering the implementation of new regional haze regulations. In addition, the new federal fine particulate standard aimed at protecting human health may require additional controls on sources contributing to secondary aerosol formation. Applying the best science available and applicable to California would help ensure that regulatory decisions are well-founded.

Field measurements concerned with the effects of air pollutant sources on visibility generally include measurements of light extinction or scattering, the mass concentrations of fine particles, and the bulk chemical composition of samples of those particles. Typically, the mass concentrations of sulfates, nitrates, elemental carbon, organic carbon, and soil particles are characterized. The total light scattering by particles, b_{sp} , is then “budgeted” as the sum of distinct contributions that are proportional to the individual species’ mass concentrations x_j :

$$b_{sp} = \sum e_j x_j.$$

This budget provides a basis for apportioning visibility management resources to focus on sources of the most important species.

The coefficient e_j in the light scattering budget is the mass-specific scattering, or “scattering efficiency,” of the j^{th} species. It depends on the species’ refractive index, density, water uptake, distribution with respect to particle size, and other factors. Its value in an actual ambient aerosol is difficult to determine because simultaneous measurements of all relevant variables are rarely available in sufficient detail. Where detailed aerosol measurements are unavailable, scattering budgets are instead often based on multiple linear regression of measured total scattering on measured species mass concentrations. The regression approach extracts estimates of the e_j from repeated measurements of b_{sp} and x_j , where the number of samples analyzed should considerably exceed the number of species. The regression estimates are characteristic of the overall set of samples and do not capture fluctuations of scattering efficiency in individual observations.

The research described here examines theoretical conditions under which multiple regression provides sound estimates of the e_j , and identifies the errors produced in regression estimates by violations of these conditions in actual California aerosols.

2.2.7.2 Methods

A new theoretical framework was developed within which regression analyses can be shown to yield unbiased estimates of the mean light scattering budget for the given collection of samples. The assumptions of the new theory are less restrictive than those in previous justifications offered for regression; those excluded situations where species’ particle size distributions and water uptakes might vary from sample to sample, as they are known to do in reality. The sole condition required by the new theory is that any variations in each species’ characteristics be random: that is, that they be statistically independent of all species’ concentrations.

The new theory yields an equation that relates errors in regression-derived scattering budgets to particular violations of the independence assumption. This equation serves as a “statistical microscope” that allows us to resolve the overall error into a sum of distinct component errors, each arising from correlated variations between efficiencies and concentrations. The individual terms in this decomposition were evaluated for a synthetic aerosol data set based on actual measurements made during the Southern California Air Quality Study (SCAQS).

In an earlier research effort, McMurry and coworkers at the University of Minnesota Particle Technology Laboratory (PTL) developed models of the SCAQS aerosol that integrated detailed measurements of particle chemical composition, water content, and size distribution in each sample. The expected total light scattering by these particles was then computed from electromagnetic theory (Mie theory) and found to exhibit reasonable agreement with actual SCAQS measurements. For the present analysis of regression, a self-consistent set of input data was constructed from the PTL work by pairing the measured species mass concentrations with the calculated total scattering coefficients. For these hybrid data, the exact relationships of scattering to particle composition are thus known *a priori*.

The mean scattering efficiencies estimated by multiple linear regression on the PTL SCAQS data were compared with the exact values defined by the PTL model. Differences were then resolved into the individual terms of the error equation described above. In this manner, it was possible to relate errors in the regression estimate for sulfate, for example, to non-random

variations in the concentrations and efficiencies of nitrate, sulfate, carbon, and soil. Table 5 gives an example of these results.

Table 5. Example results for PTL external-mixture model of SCAQS aerosol data.
All entries are in m^2/g .

	(a) mean(e_j)	(a) e_j^{reg}	(b) Nitrate	(b) Sulfate	(b) Carbon	(b) Soil
Nitrate	5.4	<u>7.5±0.6</u>	<u>1.3</u>	<u>1.0</u>	-.3	0.1
Sulfate	5.1	5.8±1.0	0.4	0.2	0.2	-.1
Carbon	5.8	4.7±0.8	-.9	<u>-.7</u>	<u>0.5</u>	0.1
Soil	2.8	<u>-.3±1.5</u>	-1.2	-1.0	-.6	-.3
<p>(a) Mean scattering efficiencies compared with regression estimates (\pm standard error). Regression estimates are underlined if disagreements are statistically significant ($p \leq 0.05$).</p> <p>(b) Decomposition of estimation errors $e_j^{\text{reg}} - e_j$. Entries in a column arise from concentration-dependent variations in the scattering efficiency of the column species; the sum of the entries in a row is the error $e_j^{\text{reg}} - e_j$ in the regression estimate for the row species. Statistically significant ($p \leq 0.05$) values are underlined.</p>						

2.2.7.3 Results and Discussion

This research identified the theoretical conditions that justify regression apportionment of light scattering and showed how deviations from these conditions caused errors in the apportionment. It examined the degree to which these conditions were satisfied for one set of data from one location and season, but did not address how generally these results apply to other situations. Further application of this method to other settings is needed to establish whether the observations noted here are representative.

The multiple linear regression approach is theoretically valid for apportioning mean scattering by externally mixed aerosols if species' scattering efficiencies are statistically independent of species mass concentrations. (An externally mixed aerosol is one in which each particle consists of a single species.) However, this condition of independence is not always met in the atmosphere. Variations in species efficiencies that correlate with variations in species mass concentrations can distort regression apportionment of mean scattering. Significant distortions were observed in the application of regression analysis to the PTL SCAQS data.

The theory can be extended to an internally mixed aerosol (i.e., one in which several species are contained in each particle). Such a mixing structure is more typical of photochemically generated aerosols. However, the attribution of scattering to an internally mixed species does not necessarily yield the quantity of practical interest, which is the scattering decrement to be expected from the reduction or elimination of a species. Moreover, the sum of the species contributions, $e_j x_j$, need no longer add to the total light scattering b_{sp} . Applying the multiple regression approach to an internally mixed model of the SCAQS aerosol produced efficiencies similar to those derived for the externally mixed aerosol.

Regression sometimes yields accurate estimates of scattering efficiency even when the statistical conditions required by theory are significantly violated. These accidental successes arise from multiple offsetting errors, and are thus unreliable. Such fortuitous agreement of regression estimate with theory is evident for organic compounds in Table 5. The agreement in this example vanished when refinements were undertaken to improve the estimates for other species.

When uncertainties are accounted for, scattering budgets based on regression-derived efficiencies are not necessarily more informative than simple budgets that equate a species' fractional contribution to scattering with its fractional contribution to fine particle mass.

The objective of this task was met.

2.2.8 Project MOHAVE Draft Final Report

Note: This work was performed as PIER DMAT Task 2.6.

Objectives:

- Prepare and circulate a draft of the Project MOHAVE final report for comment.

Deliverables:

- None

Background:

Two versions of the draft final report were prepared for circulation and comment in August and September 1998. The latter draft was also provided to the Independent Peer Reviewers for their comments.

2.2.9 Independent Peer Review

Note: This work was performed as PIER DMAT Task 2.7.

Objectives:

- Provide an independent peer review of the technical contents of the Project MOHAVE Draft Final Report.

Deliverables:

- Peer Reviewer Comments (Appendix G).

Background:

Six eminent scientists with no connection with Project MOHAVE were selected to review and provide comments on the draft final report. These scientists were:

- Dr. P. Koutrakis – Harvard University
- Dr. P. Hopke – Clarkson University
- Dr. R. Bergstrom – Bay Area Environmental Research Institute
- Dr. J. Kahl – University of Michigan
- Dr. A. Wexler – University of Delaware
- Dr. I. Sykes – Titan/ARAP

Each individual was selected because of their previous expertise in one or more areas of the Project MOHAVE assessment. Their primary responsibility was to review the draft final report and assess its adequacy in terms of two principal standards of review:

- Technical soundness – are the assumptions valid, analytical methods sound, and conclusions defensible?
- Report presentation – are the conclusions accurately and understandably conveyed by the report?

The most significant comments provided by the reviewers were:

- All reviewers were comfortable with the overall scope and preparation of the report.
- All reviewers noted the difficulties and limitations in using the tracer data to devise estimates the conversion rates of SO₂ emissions to particulate sulfur.
- There was considerable comment on the use of frequency distributions to portray the range of modeling results generated by the various investigators. A number of reviewers felt that this was inappropriate in light of the fact that the models did not agree with each other to any extent on any particular day.

Comments received from the peer reviewers were addressed individually and incorporated as appropriate into the Project MOHAVE Final Report. The peer reviewer comments are contained in Appendix G to this report.

The objective of this task was met.

2.2.10 Project MOHAVE Final Report

Note: This work was performed as PIER DMAT Task 2.8.

Objectives: Deliver the Project MOHAVE Final Report.

Deliverables:

- Project MOHAVE Final Report

Background:

The Project MOHAVE Final Report was completed and submitted to the USEPA on March 19, 1999. This milestone represented the official completion of the project. The interested reader can find the final report by visiting the USEPA Internet web site at <http://www.epa.gov/region09/air>.

2.2.11 Summary of Conclusions from Project MOHAVE

The following is a brief summary of the main findings from the Project MOHAVE Final Report. The report's Executive Summary is contained for reference in Appendix A of this report. These findings were borne out of a numerous scientific studies and analyses, including those developed from the PIER DMAT Project.

- Project MOHAVE data analysts found negligible correlation between measured MPP tracer concentrations and visibility impairment at Meadview or Hopi Point. The absence

of any obvious relationship cannot rule out MPP contributions to haze in the GCNP, but it strongly suggests that other emission sources were primarily responsible for the haze.

- Other analyses done as part of Project MOHAVE show that during the summer intensive monitoring period, there was clear observational evidence linking emissions from distant urban emission sources such as southern California to visual impairment at the GCNP.
- A number of mathematical assessment models were applied to estimate the impacts of MPP emissions on haze levels in the GCNP, but a high level of uncertainty was found among all of the model predictions. On many of the study days, for instance, the different modeling approaches did not agree on whether there was a contribution from MPP at a given receptor location on a given day. For these reasons, the results from any specific method on any specific day were not given substantial credibility.
- The most likely causes for these model discrepancies are the lack of first-hand information about the rate of formation of sulfur-containing particles, and limitations in the information available about the exact speed and direction of the winds aloft (at plume height) that transported the emissions from MPP.
- Even though the various modeling methods did not arrive at the same impact conclusions at any given time, the typical levels of impact they determined were relatively consistent between the models. These typical levels were reported in the Project MOHAVE final report in the form of cumulative frequencies, i.e., as the levels of concentrations or impacts that would be exceeded a certain percentage of the time. One should recognize that the focus on the use of frequency distributions hides the lack of day-to-day agreement between the methods as discussed above.
- From the cumulative frequency distributions, the estimated summertime contribution of MPP emissions to the measured visibility at Meadview (near the western end of the park) ranged from 0.2 to 0.6% (depending on the model) at the 50th percentile and 1.3 to 2.8% at the 90th percentile, for 12-hour averages.
- Wintertime estimates of the MPP contribution were much smaller, 0.0% at the 50th percentile and 0.1% at the 90th percentile.
- For Hopi Point, a measurement location that is well within the park and close to the main visitor area, the 50th percentile summertime estimates of the MPP contribution to visibility were in the range of 0.1 to 0.4%, and the 90th percentile values ranged from 0.5 to 2.6%.
- Wintertime estimates of visibility contributions at Hopi Point were 0.0% at both the 50th and 90th percentile.
- None of the predicted 50th and 90th percentile contributions presented in the Project MOHAVE final report would be perceptible to humans if the impairment was in the form of a uniform regional haze. The values of these contributions, up to 2.8% of measured visibility, are well below the perceptibility range of 10 to 20% presented by Pitchford and Malm (1994).
- Model predictions were made for extreme occurrences (ie., beyond the 90th frequency). However, the investigators felt that those values above the 90th percentile should be viewed skeptically because of the inability of the various modeling techniques to reach

consistent conclusions as to which days manifested the highest predicted contributions. The Project MOHAVE report cautions that extreme value estimates by any of the methods “should not be trusted as a true reflection of greatest MPP impacts.” Further, the report concluded that Project MOHAVE data analysts were unable to find any observational data to directly corroborate the extreme values predicted by some of the models.

- The meteorological conditions that occurred during the Project MOHAVE field studies during 1992 were typical of the weather patterns that normally affect transport and dispersion on the Colorado Plateau.

The most significant finding of Project MOHAVE was the lack of correlation between MPP tracer, elevated levels of sulfates, and visibility impairment at the GCNP. In other words, using actual field measurements, the project analysts were unable to correlate incidents of visual impairment or incidents of elevated sulfate with the times when the MPP tracer appeared at the park. This point is important because this conclusion is based on actual data and does not rely on model predictions that were shown to be highly uncertain. This finding is amply demonstrated in the data analyses of Mirabella and Farber (1999) which are contained in Appendix B of this report, prepared as part of the PIER DMAT Project.

2.3 California-Specific Visibility and Particulate Research

The research conducted on California-specific visibility and particulates focused on three components:

- Examining the trends in particulate concentrations, visibility, and visibility-causing emissions in California to assess the extent of visual impairment in California.
- Developing and testing an advanced plume chemistry model for future applications to point emission sources such as power plants.
- Comparatively evaluating several methods for sampling PM_{2.5}, including the USEPA Federal Reference Method (FRM), to assess the level of accuracy and uncertainty in the measurement of fine particulates. These latter research efforts were undertaken by the EPRI under the direction of SCE.

2.3.1 Trends in Visibility and Visibility-Impairing Emissions in California

2.3.1.1 Background and Objectives

Note: This work was performed as PIER DMAT Task 3.1.

Objectives:

- Document the historical trends in atmospheric particulates, visibility, and visibility-impairing emissions in California.
- Relate these trends to emission trends from the energy sector in California.
- Compile a database consisting of the air quality/emission trend data.
- Evaluate the efficacy of the present generation of mathematical models for use in performing regional visibility assessments in California.

- Provide recommendations for improving the state-of-the-science for sampling PM₁₀ and PM_{2.5}.

Deliverables:

- Contractor Report: Extent of Visual Impairment in California by ENSR Corporation (1999) (See Appendix H).

Background:

The purpose of this task was to describe the extent of visual impairment in California and to identify historical trends in visibility, visibility-impairing aerosols and emissions. Scattering and absorption of light cause visual impairment in the atmosphere by gases and particles. The total effect of scattering and absorption is called light extinction. Light extinction is usually measured in terms of the light extinction coefficient, which is the fractional reduction in light intensity that occurs over a specified distance in the atmosphere. Similarly, light scattering and absorption by particles and gases are expressed in terms of their respective light scattering and absorption coefficients. Light scattering by particles between about 0.1 and 1.0 micrometers (µm) in diameter is usually the major contributor to the light extinction coefficient, but light absorption by particles and gases can also be important. In very clean air, light scattering by air molecules (called Rayleigh scattering) can be comparable to light scattering by particles and absorption by particles and gases.

The principal focus of this task was in defining and describing California-specific visibility issues and concerns. The important issues relate to determining the nature and extent of visual impairment and its causes, and identifying analytical tools that may be applied in mitigating such impairment. Special attention in this regard was also placed on examining the role of emissions from the energy sector in California on visual impairment. This information will prove useful as decision-makers come to terms with the implementation of the 1999 USEPA Regional Haze Regulations. The data set compiled for this effort represents one of the most complete ever assembled for California.

Full details on the databases acquired, statistical analyses performed, and conclusions can be found in Appendix H.

2.3.1.2 Methods

Emissions, optical, and particulate matter data were acquired and compiled into databases for subsequent analysis. The California Air Resources Board (ARB) (1998) estimated annual average daily emissions of PM₁₀, nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO) and VOCs at five-year intervals from 1985 through 2010, categorized by standard industrial classification code and source category code within each county and air basin.

Optical and particulate matter data were available from the IMPROVE network maintained by the National Park Service and from monitoring sites operated by California local air pollution control agencies. Optical data included the light extinction (b_{ext}) and absorption (b_{abs}) coefficients measured at IMPROVE sites and the particle light scattering coefficient (b_{sp}) and coefficient of haze (COH) measured at local agency sites. Particulate matter data included PM_{2.5} mass and chemical composition and PM₁₀ mass from IMPROVE sites, as well as PM_{2.5} mass and PM₁₀ mass and chemical composition measured at local-agency sites. The available optical data

were supplemented with light scattering and extinction coefficients calculated from particulate matter data at the IMPROVE sites. The IMPROVE data were acquired from the National Park Service Air Resources Division Internet FTP server (ftp://alta_vista.cira.colostate.edu/), and the local agency data were acquired from ARB (1997).

The light extinction coefficient is measured continuously at IMPROVE sites with transmissometers and reported as hourly averages. Particulate matter samples are collected over 24-hour periods twice weekly on filters with IMPROVE samplers and analyzed by LIPM for the particle light absorption coefficient and by various techniques for mass, chemical elements, elemental and organic carbon and water-extractable ions. Sisler et al. (1996) provide details of IMPROVE procedures. The IMPROVE measurements may underestimate concentrations of semi-volatile organic compounds because of loss of material from the filter samples. The light scattering coefficient is measured continuously with integrating nephelometers at local-agency sites and reported as hourly averages. The nephelometers used at these sites generally raise the temperature of the sampled air somewhat above ambient, which can cause a reduction in relative humidity, leading to a loss of water from the particles and an underestimate of the particle light scattering coefficient. The COH is measured over two-hour periods by light transmission through samples collected on glass fiber filter tape by moving filter tape samplers. Although the coefficient of haze is not a direct measure of the particle light absorption coefficient, changes in the COH at a site should be indicative of relative changes in particle light absorption. PM_{2.5} filter samples are collected over 24-hour periods with dichotomous samplers at local agency sites and analyzed gravimetrically for mass. PM₁₀ samples are collected over 24-hour periods with high-volume samplers and analyzed gravimetrically for mass and by various methods for a limited number of chemical constituents, including water-soluble sulfate and nitrate. The collection method can lead to loss of particulate nitrate from the sample by volatilization, so the nitrate values from these sites may be lower bounds on the actual concentrations.

The data were processed in various ways prior to analysis. The data processing activities included the following:

- PM_{2.5} emissions were estimated by applying PM_{2.5}-to-PM₁₀ emission ratios to the PM₁₀ emission estimates. The PM_{2.5}-to-PM₁₀ ratios were developed and assigned to source classification codes by ARB (1999).
- IMPROVE transmissometer measurements that were made when the hourly-average relative humidity exceeded 90% were deleted to avoid periods of fog or precipitation.
- 24-hour averages (midnight-to-midnight) of the light scattering coefficient and COH measured at local agency sites and of the light extinction coefficient measured at IMPROVE sites were calculated.
- Medians and 20th and 80th percentiles of all of the 24-hour average data were calculated by season with all years combined, and medians were calculated by season during each year. Winter was defined as December, January, and February, spring as March-May, summer as June-August, and fall as September-November. December of a year was considered to be part of winter of the following year. Medians by season within each year were not calculated when fewer than half of the possible values were available in order to reduce biases caused by non-uniform measurements.

Additionally, as mentioned previously, seasonal average light scattering and extinction coefficients were calculated from IMPROVE particle light absorption coefficient and particulate matter data following the approach described by Sisler et al. (1996).

Finally, in addition to the statistical analyses described above on the emissions and air quality data, several additional studies were completed to identify the state-of-the-science regional modeling techniques that may be useful for particulate and visibility modeling in California. Also, a review was completed identifying potential improvements to the monitoring of fine particulates (PM_{2.5}).

2.3.1.3 Results and Discussion

On the basis of the information described above, the following conclusions were identified:

- The highest fine particle concentrations in California are present in locations with surrounding topography that limits dispersion. These areas include the Central Valley, the South Coast Air Basin, the San Francisco Bay area, and the Lake Tahoe Air Basin.
- The highest concentrations at these locations generally occur during the fall or winter, when periods of low inversions and low wind speeds lead to the accumulation of emitted particulate matter.
- Carbon-containing materials and ammonium nitrate are the major constituents of PM_{2.5} at the locations with the highest PM_{2.5} mass concentrations. Wood burning may be a major source of the carbon-containing materials, particularly at locations with cooler fall and winter temperatures, while the ammonium nitrate is formed from atmospheric reactions that involve nitrogen oxides and ammonia.
- Concentrations at coastal locations, such as Redwood National Park and Point Reyes National Seashore, do not vary as much with season as concentrations at inland locations, although there is a tendency for higher concentrations to occur during fall and winter than during spring and summer.
- Concentrations at Yosemite and Lassen Volcanic National Parks are highest during the summer, in contrast with the other locations, and sulfate is a larger contributor than ammonium nitrate. This behavior may be caused by summertime park visitors or by transport from the Central Valley.
- Concentrations at San Geronio Wilderness Area are highest during spring and summer, when conditions are conducive to transport of material from the South Coast Air Basin.
- Statistically significant decreases in concentrations occurred between 1989 and 1996 in several air basins. Most notable were decreases in the San Joaquin Valley during winter and at San Geronio Wilderness Area during spring, which are the times of year when concentrations are highest at these locations.
- Estimated emissions of PM_{2.5}, nitrogen oxides and sulfur oxides decreased throughout the state between 1990 and 1995. These decreases are consistent with the observed decreases in concentrations. However, decreases in concentrations did not accompany decreases in emissions everywhere.

- Coupled with the decreasing trends in particulate concentrations and particulate-causing emissions, improving trends in visibility were noted in several visibility-protected areas of California, including Redwood National Park, Yosemite National Park, Point Reyes National Seashore, Pinnacles National Monument, and San Geronio Wilderness Area.
- Emissions from energy production are small percentages of PM_{2.5}, nitrogen oxide, and sulfur oxide emissions in California, so energy production does not likely contribute substantially to decreased visibility or increased PM_{2.5} concentrations.
- Emissions from non-mobile source energy use are a larger percentage of total emissions than emissions from energy production. In particular, wood burning is a substantial contributor to PM_{2.5} emissions in cooler locations, such as the Lake Tahoe and Mountain Counties Air Basins. Therefore, emissions from non-mobile source energy use may be important contributors to reduced visibility and increased PM_{2.5} concentrations in some parts of the state.
- Recent and ongoing developments in measurement techniques for atmospheric optical parameters and particulate matter mass and constituents will also provide new information to better characterize visibility and particulate matter.
- A comprehensive air quality and emission database, compiled for this project, will be useful to other investigators for examining other visibility issues in the state.

The objectives of this task were met.

Recommendations:

- Several atmospheric models exist that can be used to better understand relationships between emissions, atmospheric particulate matter, and visibility. However, their application generally requires extensive quantities of data and experience.
- More extensive spatial coverage is needed to better understand the nature and causes of visibility and particulate matter concentrations in California. Implementation of the PM_{2.5} monitoring network in conjunction with expansion of the IMPROVE network will help provide this information in the future.

2.3.2 Dispersion and Chemical Transformation of SO₂ and NO_x in Plumes

2.3.2.1 Background and Objectives

Note: This work was performed as PIER DMAT Task 3.2.

Objectives:

- Develop an advanced point-source reactive chemistry dispersion model incorporating all of the best features (gas- and aqueous-phase chemistry, plume dynamics, aerosol dynamics, etc.) of existing models.
- Perform diagnostic and sensitivity tests of the model's performance to assess the adequacy and accuracy of its scientific formulation.

Deliverables:

Contractor Reports:

- Santos, L., Sykes, R. I., Karamchandani, P., Seigneur, C., Lurmann, F., and R. Arndt, 1999: Second-order Puff Model with Aqueous-Phase Chemistry and Aerosols, Draft Final Report prepared for EPRI, SCE, and California Energy Commission.
- Santos, L. and R. I. Sykes, 1999: File Formats (Model Technical Documentation). Draft Final Report prepared for EPRI, SCE, and California Energy Commission.
- Computer code and User Manual for the PC-SCIPUFF Model.

See Appendix I for copies of all three deliverable documents.

Background:

Reactive plume models are often used to estimate the local or short- to medium-range (i.e., up to a few hundred km) impacts of power plants or smelters on air quality. Issues of interest typically include ozone and particulate matter concentrations above the National Ambient Air Quality Standards (NAAQS), visibility degradation, and acid deposition. For example, the second-generation ROME (Seigneur et al., 1997) has been recently applied to examine the impacts of power plants on visibility in the Dallas-Fort Worth area (Seigneur et al., 1999) and the Grand Canyon (Karamchandani et al., 1998). Examples of other plume models include the first-generation Reactive Plume Model (RPM) (Stewart and Liu, 1981), the Plume Simulation of Transport and Atmospheric Reactions (PLMSTAR) model (Godden and Lurmann, 1983), and the California Puff (CALPUFF) model (Scire et al., 1997).

All the currently available reactive plume models, including those mentioned above, have some shortcomings, either in their treatment of physical phenomena or in their treatment of chemical processes. For example, most models employ a simplified treatment of plume dispersion processes and important physical phenomena such as the effect of wind shear on plume dispersion and the effect of plume overlaps (e.g., under conditions of reversal flow or merging of adjacent plumes). None of the models includes a treatment of the effect of atmospheric turbulence on nonlinear chemical kinetics.

The newer second-generation models, such as ROME and CALPUFF, attempt to address some of these shortcomings. For example, ROME incorporates an advanced treatment of plume dispersion based on a second-order closure algorithm (Sykes and Gabruk, 1997), that has been found to provide better agreement with field measurements of power plant plumes than first-order closure and Pasquill-Gifford-Turner algorithms (Gabruk et al., 1999; Seigneur et al., 1999). ROME also has a fairly complete and comprehensive treatment of the processes governing the chemistry of power plant plumes, including gas-phase chemistry, liquid-phase chemistry, gas-particle thermodynamic equilibrium, and aerosol particle dynamics. However, ROME does not account for wind shear effects. This can be a serious limitation when applying the model for relatively long transport distances. On the other hand, the CALPUFF model is a non-steady-state puff dispersion model that uses a puff-splitting algorithm to account for vertical wind shear. However, its treatment of chemistry is highly simplified. Moreover, CALPUFF includes a relatively simple treatment of dispersion (first-order closure) compared to second-order schemes that have been demonstrated to be more realistic (e.g., Gabruk et al., 1999; Seigneur et al., 1999).

More realistic puff dispersion models have been developed as a part of EPRI and Defense Threat Reduction Agency work over the last few years. The Second-order Closure Integrated

Puff model, SCIPUFF, is a state-of-the-science Lagrangian transport and diffusion model for atmospheric dispersion applications. Second-order turbulence closure is used to parameterize turbulent diffusion in the model, providing a direct connection between measurable velocity statistics and the predicted dispersion rates. This allows an accurate treatment of dispersion and the influence of turbulence on chemical rates. The model also incorporates generalized puff splitting/merging algorithms to account for wind shear effects and can be applied to multiple emission sources. The model has recently been enhanced to incorporate detailed gas-phase chemistry mechanisms. The combined puff-chemistry model, referred to as SCICHEM, was recently evaluated using data from the 1995 Southern Oxidants Study (SOS) Nashville/Middle Tennessee Ozone Study (Karamchandani et al., 1999).

Prior to this study, SCICHEM lacked a treatment of chemical transformations in the aqueous phase. This can be a serious shortcoming, since a significant amount of chemical conversion can occur in cloud or fog droplets. For example, the application of ROME to the Dallas-Fort Worth region showed that aqueous conversion played an important role in converting power plant SO₂ emissions to sulfate. SCICHEM also did not include a treatment of thermodynamic partitioning of species such as nitrate between the gas (nitric acid) and particle (e.g., ammonium nitrate) phases. Because of the different removal rates of these species from the atmosphere, this limitation can introduce errors under conditions where a significant fraction of the nitrate is present in the particle phase.

Before SCICHEM can be generally applied to study the impacts of NO_x and SO₂ emissions from California sources, it is necessary to correct these deficiencies. In the study described in this section, capabilities have been added to SCICHEM to simulate liquid-phase chemistry and gas-particle thermodynamic equilibrium. Existing modules for aqueous-phase chemistry and aerosol thermodynamics were incorporated into SCICHEM. The enhanced model was then tested for a range of conditions to determine if model results were physically and chemically consistent. The new model provides the most realistic treatment of dispersion and chemistry in a plume model that can be used for California applications. The new model is suitable for studying the impacts of NO_x and SO₂ emissions from existing and proposed plants for research and policy-relevant applications (e.g., Project MOHAVE, prevention of significant deterioration determinations). The new model can offer the public and the private sectors an alternative to CALPUFF.

2.3.2.2 Methods

The first step in implementing the aerosol thermodynamic module and aqueous-phase chemistry module into SCICHEM was to select appropriate modules to use. For aerosol thermodynamics, the objective was to identify a module that could be used to estimate the equilibrium phase distribution of sulfuric acid, sulfate, nitric acid, nitrate, ammonia, ammonium, sodium, chloride, and hydrochloric acid. Several recent studies were reviewed that compared and evaluated multiple aerosol thermodynamic modules (Kumar et al., 1998; Ansari and Pandis, 1999; Zhang et al., 1999) to guide the selection of a module for SCICHEM. Based on those reviews, we selected Simulation Composition of Aerosol Particles at Equilibrium (SCAPE2) for incorporation into SCICHEM, as it offers a comprehensive treatment of gas/particle chemical composition and thermodynamics, good accuracy, reasonable computational efficiency, and no copyright restrictions.

The requirements for the aqueous-phase chemistry module were that it should be readily available in a package with a robust numerical solver and that it should provide a relatively complete representation of the aqueous sulfur chemistry and the chemistry of the compounds that affect the sulfur chemistry. The following four aqueous-phase chemical mechanisms were considered in our review:

- Carnegie Mellon University (CMU) Mechanism (Strader et al., 1998),
- Mass Transfer with Chemical Reaction Model (MaTChM) Mechanism (Zhang et al., 1998)
- ROME Mechanism (Seigneur and Saxena, 1988)
- Regional Acid Deposition Model Version II (RADM-II) Mechanism (Walcek and Taylor, 1986)

All of the mechanisms are designed for estimation of sulfate production from SO_2 in atmospheric liquid water and include the three dominant pathways for dissolved SO_2 species (S(IV)) oxidation: hydrogen peroxide, ozone, and oxygen catalyzed by iron and manganese.

The CMU and MaTChM mechanisms incorporate the highest level of chemical detail and are very similar. The CMU mechanism includes 17 gas-aqueous equilibrium reactions, 18 aqueous equilibrium reactions, and 99 aqueous-phase kinetic reactions among 18 gas-phase species and 28 aqueous-phase species. The CMU mechanism is an updated version of the Pandis and Seinfeld (1989) mechanism. Zhang et al. (1998) compared the MaTChM mechanism to the Pandis and Seinfeld (1989) mechanism and found several missing reactions and outdated rate constants in the latter. The CMU mechanism of Strader et al. (1998) includes the updates recommended by Zhang et al. (1998). Thus, these two mechanisms are essentially equivalent.

The ROME mechanism is less detailed than the first two mechanisms. It incorporates the principal reactions controlling aqueous-phase sulfate formation in most circumstances and includes some updated reaction rates from those reported by Seigneur and Saxena (1988). The RADM-II mechanism, which is also used in the SARMAP Air Quality Model (SAQM), Multiscale Air Quality Simulation Platform (MAQSIP), and Community Multiscale Air Quality (CMAQ)/Models-3 three-dimensional air quality models, is the least detailed of the mechanisms. The CMU and MaTChM mechanisms are well suited for use in SCICHEM. Strader et al. (1998) tested seven numerical solvers and found the Variable-Coefficient Ordinary Differential Equation Solver (VODE) to be the fastest for a range of conditions. The MaTChM model uses the Livermore Solver for Ordinary Differential Equations (LSODE) solver that Strader et al. (1998) found to be three times slower than VODE. Strader et al. (1998) also tried to identify the minimum number of species that needed to be integrated in the module to increase the computational efficiency. Given that the mechanisms in the CMU and MaTChM modules are similar, and that the CMU implementation appears to be more efficient, the CMU module was selected for implementation in SCICHEM.

The next step was to implement the selected modules into SCICHEM and test the new model to ensure that implementation was correct. Testing was performed at several stages of the implementation to assess whether the software was operating as intended and responding to changes in model inputs in a manner that was consistent with scientific expectations. There were also significant changes made to the CMU aqueous-phase chemistry module before

implementing it in the SCICHEM. These modifications involved improving the code's ability to conserve mass of sulfur, nitrogen, chlorine, and carbon species.

2.3.2.3 Results and Discussion

The SCICHEM model was exercised for 40 case studies to test the newly added aerosol and aqueous-phase chemistry modules. The model's response and sensitivity to changes in model inputs were evaluated for hypothetical conditions involving a single elevated point source emitting SO₂ and NO_x under relatively constant meteorological conditions. The model's performance was evaluated on a qualitative and semi-quantitative basis. This entailed assessing whether the model's responses were directionally correct and were plausible in magnitude. No comparisons against observed data were made in the evaluation.

Plausible baseline case simulations were established with and without afternoon clouds. The results from these simulations were consistent with scientific expectations and directionally correct. For the non-cloud base case, sulfate production rates were very small. For the base case with clouds, the model predicted the expected rapid sulfate production in the aqueous phase. Furthermore, a significant fraction of the total nitrate was present in the particulate phase during the cloudy periods. This result is also expected, since at the high relative humidity, the gas-particle equilibrium for nitrate favors the formation of the particulate phase.

A number of sensitivity studies for both the non-cloud and cloud cases were conducted. For cases without clouds, the response of the model to variations in wind speeds, mixing heights, SO₂ emission rates, NO_x emission rates, temperatures, relative humidity, background ammonia concentrations, and background VOC concentrations was investigated. For the cloud cases, the sensitivity of the model was tested for changes in cloud duration, liquid water content, precipitation rate, background H₂O₂ concentrations, background ammonia concentrations, background ozone concentrations, background crustal material concentrations, background sodium concentrations, and SO₂ emission rates.

The results from these sensitivity studies showed that the model responded in a physically and chemically consistent and directionally correct manner to all the input parameter variations. For example, the model predictions of SO₂ and sulfate concentrations changed linearly in response to variations in SO₂ emission rates for simulations without clouds. For the cloud simulations, the response was less than linear near the source and linear at large downwind distances. These responses are consistent with scientific expectations. The ambient temperature and relative humidity variation sensitivity studies for the non-cloud cases showed the expected formation of particulate nitrate at low temperatures and high relative humidities, and the formation of gas-phase nitric acid at high temperatures and low and moderate relative humidities. Similarly, increasing background ammonia concentrations for the dry case resulted in some formation of particulate nitrate, in contrast with the base case study, where all nitrate was present as nitric acid.

For the cloud simulations, the model predictions of aqueous-phase conversion of SO₂ to sulfate were only slightly sensitive to variations in background H₂O₂ concentrations when the concentrations of other background species (e.g., ammonia, crustal material) influencing aqueous-phase oxidation of SO₂ were at their baseline values. Additional H₂O₂ variation sensitivity studies were conducted in which the concentrations of these other species were set

to small values, effectively eliminating all but the H₂O₂ pathway for aqueous-phase SO₂ oxidation. These studies showed that increasing background H₂O₂ concentrations resulted in higher aqueous-phase conversion of SO₂ to sulfate, particularly near the source, where SO₂ concentrations were high. At larger downwind distances, the effect was smaller because of the lower SO₂ concentrations at these distances. These results are consistent with scientific expectations.

Thus, the results from this phase of model development and testing have shown that the new aerosol equilibrium and aqueous-phase chemistry modules have been successfully implemented.

The objectives of this task were met, however, it would be highly desirable to test the model against actual field measurement test cases, further validating the fidelity of the model's scientific formulation.

Recommendations:

- Additional model sensitivity studies need to be performed using the SCICHEM plume chemistry model to identify the source of the anomalous model results uncovered during the initial model testing.
- More effort needs to be employed in testing the model against actual field measurements to provide real-world tests of model performance.

2.3.3 Quantifying Measurement Errors in Fine Particulates

2.3.3.1 Background and Objectives

Note: This work was performed as PIER DMAT Task 3.3.

Objectives:

- Investigate the extent to which PM_{2.5} measurements made with Teflon filter-based samplers differ in mass and chemical composition from aerosol particles at the point of sampling or inhalation.
- Test and compare several continuous and discrete samplers designed to quantify PM_{2.5} mass or chemical composition.

Deliverables:

Contractor Reports:

- Babich, P., Wang, P-Y., Allen, G., Sioutas, C. and P. Koutrakis, 1999: Development and Evaluation of a Continuous PM_{2.5} Mass Monitor, submitted to *Aerosol Science and Technology*, July. (*)
- Van Loy, M., Saxena, P., and Allan, M. A., 1999: Characteristics of PM_{2.5}, Sampling Method Intercomparison and Fine Particulate Composition at Six Urban Sites, Draft Final Report prepared for EPRI, SCE, and California Energy Commission, September. (*)
- Obeidi, F., Eatough, N.L., Eatough, D.J. 1999. Semi-volatile fine particulate matter at Riverside and Bakersfield, California. (Submitted to *Aerosol Science and Technology*, July 1999).

- Obeidi, F., Eatough, D.J. 1999. Continuous measurement of semi-volatile fine particulate mass in Provo, UT. (Submitted to *Aerosol Science and Technology*, July 1999).

(*) See Appendix J of this report for copies of these documents.

Background:

To assess the validity of results generated by mathematical models, it is necessary to use measurement data to provide input parameters to the models as well as to provide a basis for comparing the model results with real-world observations. Both models and measurement data have inherent uncertainties dealing with the formulation of the physical and chemical processes each try to estimate. The purpose of this task is to examine the uncertainties on the measurement side of the equation.

USEPA's prescribed FRM for PM_{2.5} mandates collection of particulate matter passing through a 2.5 µm size-selective inlet on a single Teflon filter. However, the accuracy of the FRM itself for determining aerosol mass at the point of sampling is questionable due to potential errors introduced by volatilization or condensation of inorganic and organic compounds such as ammonium nitrate and some hydrocarbons which readily partition between the gas and particle phases. Additionally, most existing PM_{2.5} data collected with FRM samplers have been gathered in rural settings. The differences in chemistry and PM composition between urban and rural settings raise questions about the adequacy of the FRM for assessing PM_{2.5} concentrations in higher population density areas.

Although particle mass is the quantity regulated by the PM NAAQS, it is far from a complete characterization of particle phase pollution. Data on particle chemical composition and size are needed to understand PM origins and sources, and to evaluate the relationships between specific chemical constituents and potential environmental and health consequences. While we are beginning to understand the limitations of the filter-based approaches, the reliability and limitations of newer automated methods remain to be explored.

This study has two main objectives: 1) investigate the extent to which PM_{2.5} measurements made with Teflon filter-based samplers differ in mass and chemical composition from aerosol particles at the point of sampling or inhalation and 2) test and compare several continuous and discrete samplers designed to quantify PM_{2.5} mass or chemical composition.

The results will have immediate value in providing more robust fine particle sampling and concentration data to be considered in the debate concerning the promulgation of the fine particle standard and the selection of the FRM. Over the longer term, by quantifying the reliability of the FRM and conventional particle sampling technology, we hope to create an impetus for improving these methods. Many private and public sector experiments in urban and nonurban locations will commence in the coming decade. These experiments will create the data needed for designating nonattainment areas and for preparing the state implementation plans (SIPs). In addition, these data can provide a useful resource to individual states and air quality districts to assess local air quality. Our study can act as a technology assessment forerunner to help design these multi-year, multi-location particle sampling networks.

2.3.3.2 Methods

PM_{2.5} mass and organic and inorganic speciation measurements were collected at sites in six cities (Riverside, CA, Chicago, IL, Dallas, TX, Phoenix, AZ, Bakersfield, CA, and Philadelphia, PA) between August 1997 and August 1998. The sites represent a cross-section of regional and climatological conditions. Riverside in August, 1997 and Philadelphia in August, 1998 are indicative of western and eastern cities, respectively, in the summer. Chicago provides data from an eastern city in the fall, although the weather was unseasonably cold and was perhaps more representative of winter. Phoenix, Bakersfield, and Dallas provide data from two western cities and one southern city during the winter. The study period in Dallas was characterized by extremely clean conditions. Precipitation was uncharacteristically frequent and heavy at Bakersfield during the study. While data from the brief sampling periods at each site (between 18 and 56 days) do not allow complete characterization of the seasonal or annual trends in aerosol composition or mass, they give a “snapshot” look at conditions that may occur.

Discrete Samplers

PM_{2.5} mass samples were collected at all six sites with a Harvard Impactor (HI) (Marple *et al.*, 1987; Marple *et al.*, 1990) operating at 10 L/min⁻¹. Several methods to quantify concentrations of PM_{2.5} inorganic ions (sulfate, nitrate, and ammonium) were employed. The Harvard-EPA Annular Denuder Sampler (HEADS) method was described and evaluated in Koutrakis *et al.* (1988), Ellestad, *et al.* (1991), and an Office of Research and Development (ORD)-USEPA publication (1992). Two HEADS samplers were used, which incorporated different backup filter configurations to capture particle phase constituents (nitrate and ammonium in Full HEADS and nitrate in the Nylon configuration) volatilized from the Teflon front filter during sampling. Only a Nylon HEADS was available at Philadelphia. Additional inorganic ion samplers were used at the Riverside and Bakersfield sites. These samplers included the Brigham Young University (BYU) Annular Denuder and ChemSpec Samplers (Annular Denuder Sampler (ADS) and ChemSpec Sampler (CSS), respectively), which both incorporate a set of sodium carbonate/glycerine-coated denuders to remove sulfur dioxide and nitric acid. The High Volume BYU Organic Sampler System (Big BOSS, Eatough *et al.*, 1995; Cui *et al.*, 1998) was also used. Finally, an experimental sampler, the Particle Concentrator-BYU Organic Sampling System (PC-BOSS, Eatough *et al.*, 1999) was also tested at Riverside and Bakersfield. This new sampler was designed to remove gas-phase carbonaceous compounds, nitric acid, and ammonia from the aerosol stream using a particle concentrator that separates the incoming airflow into minor and major flow channels. The minor flow contained concentrated particles in the 0.1 to 2.5 µm diameter range, and the major flow contained approximately 75% of the gas volume and the majority of the particles smaller than 0.1 µm in diameter. The minor flow stream passed through a carbon denuder to remove gas-phase carbon, nitric acid, and ammonia.

Several PM_{2.5} carbon samplers were also employed in this study. At Riverside and Bakersfield, the Big BOSS and PC-BOSS filters were analyzed for carbon by temperature programmed volatilization (TPV) (Cui *et al.*, 1998; Eatough *et al.*, 1989; Eatough *et al.*, 1990). At all sites except Philadelphia, two Harvard Carbon Sampler configurations were operated, one with an activated carbon paper denuder and one without (Van Loy *et al.*, 2000 in preparation). Each sampler configuration consisted of two 47-mm diameter quartz fiber filters arranged in series following an inertial impactor with a nominal particle aerodynamic diameter cut point of 2.5

µm. Only an undenuded sampler was employed at Philadelphia. The denuder in the denuded sampler was replaced with clean carbon-impregnated filter paper approximately every two weeks in an attempt to mitigate errors caused by breakthrough of gas phase organic carbon.

Continuous (In Situ) PM_{2.5} Samplers

A Continuous Ambient Mass Monitor System (CAMM) (Babich *et al.*, 1999) that measures particle mass concentrations based on the continuous measurement of the pressure drop across a porous membrane filter (Nuclepore™) was used at all sites to determine five-minute average PM_{2.5} mass. Pressure drop across the filter is proportional to the particle mass collected as a function of time, which can be integrated to obtain PM_{2.5} volume concentrations and then converted to mass concentrations by assuming a constant PM_{2.5} density. Since the sample air is passed through a Nafion™ diffusion dryer prior to its collection, the method is consistent with the FRM, which requires particle mass to be measured at a relative humidity of 40% to remove particle-bound water.

The Automated Nitrate Monitor developed by Aerosol Dynamics Inc. (ADI) (Hering *et al.*, 1999) was used to measure PM_{2.5} nitrate at Riverside. The instrument provides automated measurement of PM_{2.5} nitrate concentrations with a time resolution of 10 minutes. Analysis of collected nitrate is accomplished using a similar approach to the manual method that has been used for over 20 years to measure the size distribution of sulfate aerosols (Hering and Friedlander, 1982). However, in the ADI instrument, particle collection and analysis have been combined into a single integrated collection and vaporization cell (ICVC), which facilitates automation.

An aethalometer (Babich *et al.*, 1999) was used at all study sites to continuously (five-minute averages) measure black carbon (BC) concentrations using light absorption. BC is expected to compare well with EC measured on the quartz filter, because elemental carbon is the dominant optically absorbing material in submicron PM (Hansen and Rosen, 1990; Gundel *et al.*, 1984; Hansen *et al.*, 1984; Wolff, 1981, Allen *et al.*, 1999). The aethalometer passes ambient air through a quartz-fiber filter tape that is compared optically to a reference portion of the tape to determine the increment of light absorbing material per unit volume of sampled air. The method is described in further detail elsewhere (Hansen, *et al.*, 1984, Allen *et al.*, 1999). The model AE-16U aethalometer was used in Bakersfield, Chicago, Dallas, Phoenix and Riverside, and the model AE-20UV was used in Philadelphia.

Inorganic Gas Measurements

Three inorganic gases (sulfur dioxide, nitric acid, and ammonia) were quantified at all sites by extracting the HEADS denuders and analyzing by ion chromatography (IC). The sodium carbonate denuders captured sulfur dioxide and nitric acid, while the citric acid denuder collected ammonia.

Meteorology and Light Scattering

Air Resource Specialists collected continuous temperature, relative humidity, and nephelometry data at all sites except Philadelphia. These data were averaged over five-minute periods throughout each study period. Light scattering data were collected with an Optec NGN-2 Ambient Nephelometer equipped with a solar radiation shield and temperature and relative humidity were measured with a Rotronic MP-100F Air Temperature/Relative

Humidity Sensor equipped with and aspirated shield. Both instruments were mounted on towers at a height of approximately four meters above the ground surface. Temperature data from the Rotronic sensor and pressure data from state monitoring sites near the study sites were converted to 24-hour averages to correspond with discrete sampler collection periods. These averages facilitated calculation of pollutant concentrations at ambient temperature and pressure.

2.3.3.3 Results and Discussion

PM_{2.5} speciation data based on discrete sampler measurements at the study sites challenge some widely held paradigms regarding particulate matter composition in the United States. Sulfate is typically assumed to account for about one third of the mass of PM_{2.5}. The results of studies in various rural areas of the United States have reinforced this assumption. Furthermore, these studies reported a fairly lower fraction of particle-phase organics (e.g., about 13% in Southeastern Aerosol and Visibility Study) and negligible contributions from nitrate. In contrast to the rural PM_{2.5} data, the largest sulfate fraction measured was 36% at Philadelphia, with the next highest fractions as 19% at Chicago, 15% at Dallas, and 13% at Riverside. The other two western cities (Bakersfield and Phoenix) had sulfate fractions smaller than 6%. Organics comprised a much larger fraction than sulfate at all sites sampled, ranging from 36% at Chicago to 54% at Phoenix and Philadelphia. Nitrate was also a more dominant PM_{2.5} component relative to results from rural studies: about 12% in Dallas; more than 15% in Riverside, Chicago, Philadelphia, and Phoenix; and almost 29% in Bakersfield. Only Philadelphia had a trivial contribution from nitrate: 2.9%.

The higher concentrations of PM_{2.5} components that may undergo labile gas-particle exchange under sampling conditions (i.e., nitrate and organics) observed in this study highlight the potential pitfalls of PM_{2.5} mass samplers that rely on a single, undenuded Teflon filter with no backup filter. Such samplers are suspected to lose a substantial fraction of PM_{2.5} nitrate during sampling and equilibration of the filters prior to weighing. Losses of nitrate were observed from the HI of less than 10% on a whole study average of the nitrate collected on the Nylon HEADS. The largest losses (approximately 35% of the Nylon HEADS nitrate) were observed in Riverside, where nitrate concentrations were relatively high and ambient temperatures were elevated. The other sites experienced little or no nitrate loss on the HI. In areas where the nitrate fraction is substantial and temperatures are higher, this volatilization from a Teflon filter-based sampler could lead to errors on the order of 10% in the quantification of PM_{2.5} mass and relative contribution of other components to the total mass observed (Van Loy *et al.*, 1999 in preparation, Obeidi *et al.*, 1999 in preparation, Pang *et al.*, 1999 in preparation).

Loss of organics from Teflon filters (which includes FRM samplers) is less well understood. Teflon has a low adsorption capacity for most organics (relative to quartz or carbon impregnated filters). Thus, Teflon filters are not likely to trap as much organic compound mass that could volatilize from collected particles as would quartz filters. For the same reason, they are also unlikely to capture much gas phase organic material during sampling. Some loss of PM_{2.5} OC is likely while the filter is equilibrated in preparation for weighing, but this effect has not been quantified. Because of these unknowns, our study did not quantify OC from the Harvard Impactor sampler, but operated several quartz fiber filter carbon samplers (Van Loy *et al.*, 2000 in preparation).

The analysis of carbon sampling methods indicates that a single undenuded quartz fiber filter gives similar results to the sum of two quartz filters in series behind a carbon denuder. Use of a quartz filter following a Teflon filter to adjust the OC collected on an undenuded quartz fiber filter at Bakersfield gives a slightly lower estimate of particle-phase OC. The smaller estimated PM_{2.5} concentrations obtained from this estimate may reflect the amount of gas-phase VOC adsorption that occurs on an undenuded quartz filter. The results at Bakersfield indicate that the magnitude of this error is approximately 7%. Correction of the OC collected on a quartz filter for VOC adsorption using the OC mass collected on a back-up filter behind the first quartz filter underestimates PM_{2.5} OC relative to all of the other methods tested by approximately 20-25%.

In currently employed sampling systems, uncertainties in denuder efficiency for removing gas-phase organics and in collection efficiency of quartz or other filter media for particle-phase organics severely hinder accurate characterization of OC in PM_{2.5} (Turpin et al., 1994; Turpin et al., 1999). Our work indicates that the best currently available sampling technology for OC may be an undenuded quartz filter. In such a sampling system, volatilization of PM_{2.5} OC during sampling should be minimized, because the gas-particle equilibrium present in ambient air is not perturbed during sampling by removing the gas phase in a denuder.

Continuous/automated instruments were also compared for analysis of PM components or characteristics. HEADS, ADS, CSS, and PC-BOSS nitrate data are closely correlated with the ADI automated nitrate sampler data at Riverside. However, the ADS, CSS and PC-BOSS nitrate concentrations were all lower than the ADI sampler. This result is consistent with observed disagreements between HEADS and these samplers. Combination of discrete sampler elemental carbon and aethalometer black carbon data from all sites gives a Pearson correlation coefficient of 0.97 and a regression slope of 1.26 ± 0.05 .

Comparison of nephelometer and Harvard Impactor data reveals substantial scatter for the study overall. However, at each individual site, the correlation coefficients for HI mass and the scattering coefficient were somewhat closer to one. Significant differences in the regression slopes occurred between Riverside and both Chicago and Bakersfield. Phoenix was not significantly different than Riverside or the other sites. Reasons for these site-to-site differences are unclear, but may be related in part to temperature and humidity differences. Dallas had an extremely low regression slope with a significant y-intercept (possibly linked to the low PM_{2.5} concentrations that occurred there during the study period).

Correlations between hourly averages of data from the continuous samplers were also examined. Correlation coefficients (r_{pearson}) for the aethalometer-CAMM comparisons vary between a low of 0.32 at Riverside and a high of 0.75 at Phoenix. Riverside and Bakersfield had the smallest fractions of PM_{2.5} mass attributable to black carbon. One-hour average CAMM mass and nephelometer b_{scat} measurements were correlated with r_{pearson} greater than 0.7 at all sites except Dallas. The individual site Deming regression slopes vary between approximately 0.04 and 0.2 for CAMM-aethalometer data and between approximately 2.5 and greater than 9 for the CAMM-nephelometer correlation. All sites except Phoenix had slopes lower than 0.1. It appears unlikely that a coherent correlation between light scattering or PM_{2.5} black carbon and CAMM mass would exist over longer periods or for combined data collected under different geographical or seasonal conditions.

In summary, our results indicate that EPA's FRM for PM_{2.5} sampling does have significant limitations. It cannot assess the chemical composition of the collected aerosol and it may be susceptible to sampling errors based on gas-particle partitioning of volatile organics and nitrate under certain conditions. In high nitrate areas, as found in many urban areas in California, a significant potential for underestimation of PM_{2.5} mass concentrations exists. Additionally, if chemical speciation were performed on FRM samples in an effort to identify sources of elevated PM levels, the loss of volatile material is likely to lead to overestimation of the importance of nonvolatile components such as sulfate and elemental carbon, while underestimating organics and nitrate. Clearly, care must be taken in interpreting FRM PM_{2.5} sampling data and using them to design and implement effective and rational PM mitigation strategies.

The objectives of this task were met.

Recommendations:

- Our observations highlight the need for a more robust sampling system for carbon in airborne particles that measures the gas-particle partitioning as it exists in an unperturbed air parcel.

2.3.4 Synthetic Images Depicting Changes in California Visibility

2.3.4.1 Background and Objectives

Note: This work was performed as PIER DMAT Task 3.4.

Objectives:

- Compile onto a compact disc the Winhaze visual air quality modeler image software program and base images for several national parks in the United States, including the GCNP and Yosemite National Park in California.

Deliverables:

- A compact disc containing the Winhaze program and images along with user instructions for exercising the software (See Appendix K).

Background:

The USNPS has funded the development of a computer software package, Winhaze, that can be used to display images on a computer screen depicting the changes expected in scenic visibility as a result of changes in atmospheric particulate levels. These images are of generic value in demonstrating the perceptibility of different levels of visibility change to the human eye, and put into visual perspective what the mathematical models of plume aerosol formation produce as numerical results. Several locations are included in the Winhaze package; among them are the GCNP and Yosemite National Park in California.

2.3.4.2 Methods

The basic methodology behind the Winhaze program is to collect photographs of extremely clean pollutant-free periods and employ radiative transfer and digital image processing techniques to create synthetic imagery simulating various light extinction scenarios. The complete methodology is described in the Project MOHAVE Final Report (Pitchford, et al., 1999).

The objectives of this task were met.

3.0 Conclusions and Recommendations

3.1 Conclusions

The Energy Commission PIER transition-funded DMAT Project has resulted in the generation of a number of research products aimed at providing a more complete understanding of complex nature of visibility and its impairment. These products have used a wide spectrum of analyses, including mathematical modeling, statistical analyses of data, and comparative evaluations of several particulate matter sampling technologies.

The PIER DMAT Project was subdivided into two research areas: 1) completion of Project MOHAVE; and 2) California-specific visibility and particulate research. Project MOHAVE, initiated in 1991 and completed in 1999, was designed to quantify the relative contribution of air emissions from SCE's MPP on visual impairment at the Grand Canyon National Park. During the latter portion of Project MOHAVE, a number of knowledge gaps were identified concerning deficiencies in the methods that were being employed for quantifying MPP's impacts on visibility. Addressing these knowledge gaps was an important focus of the PIER DMAT Project.

Conclusions have been divided into the two research areas, with a reiteration of the objectives preceding the results.

Project MOHAVE

Objectives:

- Completion of Project MOHAVE Final Report and supporting research studies including:
 - Developing methods to assess the accuracy of mesoscale meteorological models that will best describe the transport and dispersion of MPP emission plumes in the complex terrain of the Colorado Plateau.
 - Applying a reactive plume model to quantify the relative contribution of emissions from MPP and other regional emission sources to particulate sulfur and visual impairment at the GCNP.
 - Quantifying the changes that would occur in particulate sulfate and light extinction at the GCNP as emissions from MPP change.

Conclusions:

The Project MOHAVE research area consisted of a number of linked studies with the results of one study feeding into the next. For example, one of the wind fields evaluated during the PIER DMAT Project provided basic input data to the reactive plume chemistry model task. The output from the reactive plume chemistry model task then provided information on particulate plume concentrations for various chemical constituents. These plume particulate values then provided the necessary information to another PIER DMAT task to develop estimates of plume impacts on visibility. These results, along with the research developed by other groups, were then integrated into the Project MOHAVE Final Report, the final PIER DMAT task for the Project MOHAVE research area.

From an overall perspective, the key conclusion from Project MOHAVE was that no observational relationships could be found linking emissions from MPP, as represented by a unique tracer, and visual impairment at locations within the GCNP. There was, however, clear observational evidence linking emissions from distant source regions such as southern and central California, northern Mexico, and nearby Las Vegas to visual impairment at the GCNP. Several different modeling methods were applied to understand the range of potential impacts from MPP. One of these models, the ROME reactive plume model, was applied as part of the PIER DMAT Project. This method incorporated comprehensive treatments of plume dynamics and chemistry to predict the conversion of SO₂ emissions from MPP to particulate sulfur in the atmosphere. Using this reactive plume model, it was found that:

- The estimated contribution of MPP to total 12-hour average sulfate concentrations measured at Meadview (at the western end of the GCNP) ranged from less than 1% to 19% from all emission sources for the time periods examined. Over the entire period, the estimated average MPP contribution to 12-hour average sulfate concentrations was about 5%.
- At Hopi Point (located near the GCNP visitor's center) MPP sulfate concentrations were smaller than those at Meadview. The estimated MPP contribution to observed 12-hour average sulfate ranged from less than 1% to 6%.
- The MPP plume had significant interactions with clouds only during one time period (during the night of August 5, 1992) as it traveled to Meadview. These trajectories were fast-moving and had short residence times and impact times at Meadview. None of the trajectories from MPP to Hopi Point encountered clouds at plume levels.

Large differences in predicted sulfur impacts from MPP were noted among the various models employed during Project MOHAVE, particularly during the infrequent conditions involving cloud/plume interactions. The principal reason for these differences relates to the chemical treatment of cloud interactions with the MPP emission plume assumed in each model.

Using the results from the reactive plume model, estimates were made using Mie theory of the effect of reducing the particulate sulfate produced by the MPP SO₂ plume on light scattering. This study found that:

- Calculations of the effect of the removal of MPP emissions found that a 19% decrease in ambient sulfate, the largest value predicted by the reactive plume model, would produce a decrease in light extinction of between 3.3% and 5.3%, depending on the assumed effect on the sulfate size distribution.
- For the entire period simulated by the reactive plume model, the decrease in light extinction is estimated to be about 1% of the total. The sulfate formation process that produced the 19% estimate in the model involves gas-phase surface reactions of SO₂ on existing particles.
- Mie theory calculations based on the size distribution effects of this process indicate that the dry extinction efficiency of the removed sulfate is in the vicinity of 2 m²/g. This value is considerably smaller than the value of 3 m²/g that is typically used to represent sulfates.

California-Specific Visibility and Particulate Research

Objectives:

- Examine the trends in historical measurements of visibility and atmospheric particulates as related to historical trends in visibility-impairing emissions in California.
- Comparatively evaluate a number of methods for sampling PM_{2.5}.

Both federal USEPA and regional/state air quality regulators are considering the implementation of new regional haze regulations. In addition, the new federal fine particulate standard aimed at protecting human health may require additional controls on sources contributing to secondary aerosol formation. Applying the best science available and applicable to California would help assure that regulatory decisions are well founded. The methods and techniques developed during Project MOHAVE have provided a technical backdrop for assessing the current state-of-the-science for visibility. However, as is inevitable in a large scientific enterprise, Project MOHAVE also exposed the limitations of existing analysis and assessment methods and thus created a focused effort for improving these methods for applications to California visibility issues.

The research conducted on California-specific visibility and particulates focused on three components:

- Examining the trends in particulate concentrations, visibility, and visibility-causing emissions in California to assess the extent of visual impairment in California.
- Developing and testing an advanced plume chemistry model for future applications to point emission sources such as power plants.
- Comparatively evaluating several methods for sampling PM_{2.5}, including the USEPA FRM, to assess the level of accuracy and uncertainty in the measurement of fine particulates. These latter research efforts were undertaken by the EPRI under the direction of SCE.

Conclusions:

- Statewide trends in particulate concentrations in many air basins showed statistically significant decreases from 1989 to 1996, consistent with the decreasing statewide trends in particulate, oxides of nitrogen and sulfur dioxide emissions.
- Improving trends in visibility were also found in several visibility-protected areas of the state including South Lake Tahoe, Yosemite National Park, Pinnacles National Monument, Redwood National Park, Point Reyes National Seashore, and San Geronio Wilderness Area.
- Emissions from the state's energy production sector were found to be small percentages of statewide particulate, oxides of nitrogen and sulfur dioxide emissions, and therefore are not thought to contribute substantially to reduced visibility or increased particulate concentrations.
- The USEPA's FRM for sampling PM_{2.5} was found to have significant technical limitations.
 - For example, the FRM cannot assess the chemical speciation of the collected aerosol, and it may be susceptible to sampling errors based on gas-particle partitioning of

- volatile organics and nitrates under certain conditions, perhaps up to 10% in the quantification of PM_{2.5} mass and relative contribution of other components to the total mass.
- In areas such as southern California where nitrate and organic particulates are major fractions of the PM_{2.5}, a significant potential for underestimation of PM_{2.5} mass concentrations exists.
 - Additionally, if chemical speciation were performed on FRM samples in an effort to identify sources of elevated PM levels, the loss of volatile material would likely lead to overestimation of the importance on nonvolatile components such as sulfate and elemental carbon while underestimating organics and nitrates.
 - The best available sampling technology for organic carbon may be an undenuded quartz filter that minimizes volatilization of organic carbon by not perturbing the gas-particle equilibrium present in the ambient air during sampling by removing the gas phase in a denuder.
- PM_{2.5} speciation data based on discrete sampler measurements at the study sites challenge some widely held paradigms regarding particulate matter composition in the United States.
 - Sulfate is typically assumed to account for about one third of the mass of PM_{2.5}. The results of studies in various rural areas of the United States have reinforced this assumption. Furthermore, these studies reported a fairly lower fraction of particle-phase organics (e.g., about 13% in Southeastern Aerosol and Visibility Study) and negligible contributions from nitrate.
 - In contrast to the rural PM_{2.5} data, the largest sulfate fraction measured was 36% at Philadelphia, with the next highest fractions as 19% at Chicago, 15% at Dallas, and 13% at Riverside. The other two western cities (Bakersfield and Phoenix) had sulfate fractions smaller than 6%.
 - Organics comprised a much larger fraction than sulfate at all sites sampled, ranging from 36% at Chicago to 54% at Phoenix and Philadelphia.
 - Nitrate was also a more dominant PM_{2.5} component relative to results from rural studies: about 12% in Dallas; more than 15% in Riverside, Chicago, Philadelphia, and Phoenix; and almost 29% in Bakersfield. Only Philadelphia had a trivial contribution from nitrate: 2.9%.
 - The higher concentrations of PM_{2.5} components that may undergo labile gas-particle exchange under sampling conditions (i.e., nitrate and organics) observed in this study highlight the potential pitfalls of PM_{2.5} mass samplers which rely on a single, undenuded Teflon filter with no backup filter.
 - Revision of our understanding of the composition of PM_{2.5} has additional implications beyond accurate sampling of airborne aerosol mass. Because the various components of PM_{2.5} have different dominant sources, accurate characterization of aerosol composition is necessary to design effective emission management strategies.
 - Finally, a new and advanced air quality model was developed that can be used to simulate the formation of atmospheric aerosols and photochemical ozone from point

sources such as power plants. This model has undergone preliminary testing, but additional work needs to be done before the model can be applied on an operational basis.

3.2 Recommendations

A number of areas for further research were identified during the course of this study. These include:

From Project MOHAVE

- Further work on understanding the uncertainties of the TP method for comparing wind fields is desirable. A question deserving attention is the sensitivity of the results to receptor spacing, especially in the case where the receptors are so far apart that the plume could pass between two of them undetected. There is clearly a receptor spacing beyond which the TP method's results will be highly uncertain. Further refinement of the method, particularly for use with three-dimensional trajectories, should be undertaken. In addition, if tracer measurements aloft become available, it would be desirable to test the full three-dimensional formulation of the method.
- In performing complex plume chemistry simulations, it is extremely important to have available measurements of pollutant concentrations at plume heights consisting of ozone, NO_x, H₂O₂, OH radical, water vapor, ammonia, and trace metals such as manganese and iron. All of these parameters play crucial roles in determining the rate of conversion in a plume of SO₂ emissions to particulate sulfur in the atmosphere.
- Obtaining high time resolution pollutant data is a necessary prerequisite in attempting to quantify air quality impacts from emission sources. This includes gaseous pollutant data as well as aerosol mass and aerosol chemical speciation data. In Project MOHAVE, for instance, the shortest averaging time available for data collection was 12 hours. This length of time made for a very difficult model simulation problem as no pollutant information was available to examine the diurnal patterns of plume dispersion and chemistry. To the extent possible within resource constraints, emission source attribution projects need to strive for hourly averaged data. Instruments to continuously monitor (i.e., approximately one hour or less) all the principal components of particulate aerosols are presently under development and should be available for operational use in the next few years.

From California-Specific Visibility and Particulate Research

- Additional model sensitivity studies need to be performed using the SCICHEM plume chemistry model to identify the source of the anomalous model results uncovered during the initial model testing. Also, more effort needs to be employed in testing the model against actual field measurements to provide real-world tests of model performance.

4.0 Glossary

ADI	Aerosol Dynamics Inc.
ADS	Annular Denuder Sampler
ARB	Air Resources Board (California)
BC	Black Carbon
Big BOSS	High-Volume BYU Organic Sampler System
BYU	Brigham Young University
CAA	Clean Air Act
CALMET	California Meteorological Model
CALPUFF	California Puff Model
CAMM	Continuous Ambient Mass Monitor System
CBM IV	Carbon Bond Mechanism Version IV
CEC	California Energy Commission
CMAQ	Community Multiscale Air Quality Model
CMU	Carnegie Mellon University
CO	Carbon Monoxide
COH	Coefficient of Haze
CPUC	California Public Utilities Commission
CSS	ChemSpec Sampler
DMAT	Desert and InterMountain Air Transport Project
EC	Elemental Carbon
EK	Enger-Koracin
ELSIE	Elastic Light Scattering Interacting Efficiencies
EPRI	Electric Power Research Institute
Fe	Iron
FRM	Federal Reference Method
FTP	File Transfer Protocol
GCNP	Grand Canyon National Park
GCVTC	Grand Canyon Visibility Transport Commission

H₂O₂	Hydrogen Peroxide
HEADS	Harvard-EPA Annular Denuder Sampler
HI	Harvard Impactor
HOTMAC	Higher Order Turbulence Model for Atmospheric Circulation
IC	Ion Chromatography
IMPROVE	Interagency Monitoring of Protected Visual Environments
IVIC	Integrated Collection and Vaporization Cell
LIPM	Laser Integrating Plate Method
LSODE	Livermore Solver for Ordinary Differential Equations
M³	Cubic Meter
MAQSIP	Multiscale Air Quality Simulation Platform
MaTChM	Mass Transfer with Chemical Reaction Model
MM5	Mesoscale Model Version 5
Mn	Manganese
MOHAVE	Measurements of Haze and Visual Effects
MOUDI	Micro Orifice Uniform Deposit Impactor
MPP	Mohave Power Project
NAAQS	National Ambient Air Quality Standards
ng	nanograms
NH₃	Ammonium
NO_x	Oxides of Nitrogen
O₂	oxygen molecule
O₃	Ozone
OC	Organic Carbon
OH	Photochemical reaction product consisting of an atom of oxygen and an atom of hydrogen
ORD	USEPA Office of Research and Development
PAN	Peroxyacetyl Nitrate, an eye irritant photochemical reaction product
PC-BOSS	Particle Concentrator - BYU Organic Sampling System

PIER	Public Interest Energy Research
PLMSTAR	Plume Simulation of Transport and Atmospheric Reactions
PM	Particulate Matter (subscripts 2.5 and 10 refer to particulate with an aerodynamic diameter less than 2.5 microns and 10 microns, respectively)
PTL	Particle Technology Laboratory (University of Minnesota)
RADM-II	Regional Acid Deposition Model Version II
RAPTAD	Random Puff Transport and Diffusion Model
ROME	Reactive and Optics Model of Emissions
RPM	Reactive Plume Model
SAQM	SARMAP Air Quality Model
SARMAP	San Joaquin Valley Air Quality Study (SJVAQS)/ Atmospheric Utility Signatures Predictions and Experiments (AUSPEX) Regional Model Adaptation Project
SCAPE2	Simulation Composition of Aerosol Particles at Equilibrium
SCAQS	Southern California Air Quality Study
SCC	Source Category Code
SCE	Southern California Edison
SCICHEM	Second-order Closure Integrated Puff model with Chemistry
SCIPUFF	Second-order Closure Integrated Puff model
SIC	Standard Industrial Classification
SIP	State Implementation Plan
S(IV)	Dissolved SO ₂ species
SO₂	Sulfur Dioxide
SOS	Southern Oxidants Study
SO_x	Oxides of Sulfur
TP	Tracer Potential
TPV	Temperature Programmed Volatilization
USEPA	United States Environmental Protection Agency
USNPS	United States National Park Service

VODE

Variable-Coefficient Ordinary Differential Equation Solver

VOC

Volatile Organic Compound

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APPENDIX A

EXECUTIVE SUMMARY, PROJECT MOHAVE FINAL REPORT, SUBMITTED TO THE USEPA
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APPENDIX B

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APPENDIX G

PROJECT MOHAVE FINAL REPORT INDEPENDENT PEER REVIEW COMMENTS

APPENDIX H

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APPENDIX I

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APPENDIX J

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COMMISSION, SEPTEMBER

APPENDIX K

WINHAZE VISUAL MODELING PROGRAM AND PROJECT MOHAVE IMAGES

Appendix I — Diffuse Reflective Torchiere Study

How do a material's reflectivity and specularity affect fixture efficiency? To determine this relationship, the reflectivity and specularity of several typical lighting fixture materials was studied. White paint and Alcoa's Miro aluminum were chosen as sample fixture materials for their spectrum of reflectivity and specularity and because they are readily available. Six identical torchieres were built, three with white paint and three with Miro. The white paint fixtures included flat, semi-gloss and high-gloss paint, keeping the reflectivity constant and changing the specularity with each fixture. Paint is not measured in specularity percentages but with a gloss meter, which indicates the specularity at 60 degrees from the material. Three fixtures, the same shape as the white paint fixtures, were built with a spectrum of Miro aluminum, Miro 1: Extra Bright Rolled, Miro 5: Reflector diffuse and Miro 9: Stucco G. Table I-1 provides reflectivity data on each fixture.

Table I-1 Published Reflectivity and Specularity of Experimental Materials

Material	Description	Gloss Meter	Total-Reflection	Diffuse-Reflection
White 1	Flat	0-10	~80	
White 2	High-Gloss	80-100	~80	
White 3	Semi-Gloss	40-60	~80	
Miro 5	Reflector Diffuse		94	77-88
Miro 1	Extra Bright Rolled		95	3
Miro 9	Stucco G		95	94

Each of the six fixtures were photometrically analyzed in the Lawrence Berkeley National Laboratory goniophotometer with a 22 watt Philips T5 lamp, in a torchiere, as shown in Table I-2. Experimental reflectivity and specularity data were measured with the Minolta Reflectometer.

Table I-2 Photometric Data

File Name:	miro9.xls	miro5.xls	miro1.xls	whitep1.xls	Whitep3.xls	whitep2.xls
	95% reflective	95% reflective	95% reflective	Flat	Semi-Gloss	High-Gloss
Diffusivity:	94% diffuse	77-88% diffuse	3% diffuse	Gloss Meter 0-10	Gloss Meter: 40-60	Gloss Meter 80-100
Goniometer Test:						
Power (Watts)	45.98	42.61	43.72	47.50	45.28	44.20
Total Lumens	2470	2360	2540	2380	2300	2170
Fixture Efficacy (lm/W)	54	55	58	50	51	49
Bare Bulb Efficacy(lm/W)	74.91	74.91	74.91	74.91	74.91	74.91
Efficiency:						
Efficiency (%)	72%	74%	78%	67%	68%	65%
Sphere Test:						
Power (Watts)	46.96	46.96	46.96	46.96	46.96	46.96
Bare Bulb Lumens	3518.07	3518.07	3518.07	3518.07	3518.07	3518.07

The fixture efficiencies of the white paint fixtures do not appreciably vary from the use of flat, semi-gloss, or gloss type paint. Some differences in efficiency can be seen among the Alanod fixtures.

From this data, it was concluded that using highly spectral, highly reflective materials would boost total lumen outputs by as much as 15 percent, closely matching the reflectivity differences between the materials used. This information could be used along with materials cost issues to determine whether the added cost of using highly reflective materials to boost lumen outputs is economically justifiable. Factors included not only the added cost of the high performance reflector materials, but also the added manufacturing steps (such as stamping, forming, adhesion) necessary to implement these materials.

Appendix II Test Results

Approximately 50 goniophotometric tests were performed at the Lawrence Berkeley National Laboratory on the various prototypes and reflector geometries. Additionally, integrating sphere tests were used to determine total bare bulb lumen outputs. Data from both series of tests was used to determine the performance characteristics of the new designs.

Table II-1 provides a list of the Excel file data sheets of the goniophotometric tests. The list identifies the prototype names with the file names (i.e. Opala-t2b1 is called Prototype1 in this report).

Table II-1 Goniometric Data Sheets

Prototype 1	Prototype 2	Prototype 4	GE 60W Profile
1. Opala-t2b1	18. Willy-t2b3	30. Aat2	39. Ge2d0899
2. Opal-t2b00	19. Willy-t2b0	31. At1	
3. Opal-t2b0-1	20. Willy-t1b4	32. Aet1	Emess 55W
4. Opalb-t2b0	21. Willy-t0b5		40. Emess1
5. Opal-t2b01	22. Willy-t0b4	Prototype 5	
6. Opal-t2b0	23. Willy-t1b3	33. Icebox2	Reflector Study
7. Opal-t3b0	24. Willy-t2b4	34. Icebox3	41. Miro1
8. Opal-t1b0		35. Icemd	42. Miro5
9. Opalc-t1b3	Prototype 3	36. Icemw	43. Miro9
10. Opal-t1b1	25. Tiff-close	37. Iceww	44. Whitep1
11. Opal-t1b3	26. Tiff-clos1		45. Whitep2
12. Opal-t2b3	27. Tiff-quart	Prototype 6	46. Whitep3
13. Opal-t1b1	28. Tiff-clos	38. Perry3	
14. Opal-b2b3Tiff-close	29. Tiff-half0		
15. Opal-t0b1-1			
16. Opal-t0b1Tiff-clos1			
17. Opal-t0b2			
Opal-t0b3Proto 2			